A THESIS

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Investigations of the Vibrational Spectra
of a Number of Related
Quinonoid and Benzenoid Compounds.

ABSTRACT

The vibrational spectra of a number of chloroquinones, hydroquinones, benzenediazo-oxides and aminophenols have been recorded and complete assignments attempted. In the case of two chloroquinones, p-hydroquinone and p-aminophenol the previous assignments for these compounds have been reviewed and modified in the light of more extensive experimental data, such as information obtained from the far infrared region, comprehensive Raman spectra and deuteration experiments.

The planar and non-planar vibrational frequencies of parabenzoquinone have been calculated using various sets of zero-order force constants. Using a least squares method the refinement of the initial sets of force constants was carried out with the help of the observed frequencies of parabenzoquinone and some of its deuterated derivatives. The resulting sets of force constants were used to calculate the vibrational frequencies of other compounds considered in this work. The potential energy distribution and Cartesian displacement figures calculated from these and other zero-order force fields have been used to aid the assignment of the spectra.

The n.m.r. spectra of some of the compounds considered here have been recorded and a complete analysis of the spectrum of p-benzenediazo-oxide has been carried out.

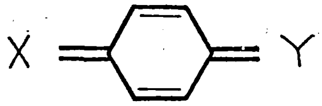
CONTENTS

Chapter I.

1. General Introduction

Molecular systems containing interacting centres of electron density have for some time been the source of a great deal of interest to many chemists. Innumerable pieces of research are described in the literature by chemists looking at these systems from a number of different angles. One such system which has always occupied a special place, particularly to the physical organic chemist, is the para-substituted six membered aromatic carbon ring.

In the special case where one has substituent X and Y in an aromatic molecule p-X-C_6H_4-Y, and if X and Y fulfil certain conditions regarding their relative electronegativities and π-bonding capabilities etc. then the electron density distribution is modified in the sense indicated by the contribution of resonance forms such as I:



. I

When this structure is a predominant or at least an important contribution to the overall electronic structure then it follows that our molecule is no longer purely aromatic but is more or less modified (quinonoidal) depending upon the importance of structures such as I. It is clear that large contributions from such structures will give rise to a number of changes in the properties of this system as compared to other structurally similar molecules in which resonance forms, such as I, are unimportant.

Let us consider the influence of the interactions examplified by structure I on the vibrational spectrum of the molecule p-XC_6H_4Y. The vibrational spectrum of a molecular system in equilibrium at ordinary temperature and pressure is determined primarily by the following factors:

1. the way in which the atoms are arranged in the molecule or the geometry of the molecule together with the masses of the atoms;
2. the types of forces that bind the adjacent atoms together; and
3. the medium in which the molecule exists.

The first factor may be made relatively constant if one is confined to a set of closely related molecules, the third is expected to vary appreciably from one molecule to another in the same medium only if strong intermolecular interactions can come into play. The second factor concerns the σ-and π-bonding arrangements within the molecule. It has been repeatedly stated by a number of authors that the σ bond skeleton plays a greater part in determining the vibrational spectrum of a given conjugated molecule[48]. The part played by the π-bonding structure is by no means negligible, however.

The influence of the two major types of bonding is not always easy to separate and observed changes in the vibrational spectrum of a series of related molecules cannot always be attributed to specific changes in the bonding arrangements within the molecule. Nevertheless it has been shown that it is possible to draw some useful conclusions and make certain qualitative assertions regarding the causes and mechanisms of changes in the vibrational spectra of aromatic molecules from comparative studies of structurally related compounds[49].

One of the principal drawbacks of this type of study is that it is based on the tacit assumption that changes in the stretching frequency of the bond C-X, say; which are observed when the substituent Y is changed are due almost entirely to electronic interactions between these substituents which are transmitted via the σ and π bond structure of the molecule.

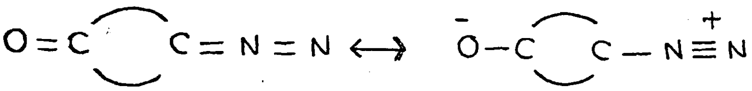
This obviously ignores the fact that a vibration in a certain part of the molecule in question does not take place independently but is in most cases coupled to vibrations in other parts of the molecules which take place simultaneously. The magnitude of the coupling is of course influenced by a number of factors which need not remain constant even when one is comparing structurally similar molecules.

These coupling effects must be taken especially seriously when the difference between the frequencies of the vibration in question and other vibrations in the molecule is of the order of 200 cm^{-1} or less. Such is the case for instance when we consider the series p-OHC_6H_4Y, Where Y = $-NH_2$ -OH, NO_2 etc. since here both the CO and C-Y stretching frequencies will be in close proximity to at least two C-C stretching vibrations.

It therefore seems that studies aimed at achieving a better understanding of the influence of electronic interactions on the vibrational spectra of conjugated molecules should ideally consider the vibrational spectrum as a whole and should also be supplemented by calculations of potential energy distribution figures and/or Cartesian displacement vectors which should provide a more complete picture of the vibrational problem being considered. This, of course, provided that the force field on which these calculations will have to be based is at least a reasonable one. The present work is primarily intended as a study of the vibrational spectra of para-quinonoid and benzenoid systems whose substituents are known to give rise to some conjugation across the carbon ring. An important example of such compounds are the p-benzene diazo-oxides for each of which it is possible to draw two principal structural formulae.

The structure of the diazo-oxides has been the subject of intermittent debate since the beginning of this century Bambergen[1] (1895) and Morgan et al[2] (1915) assumed ortho- and para-rings to be involved while Wolff[3] (1900) favoured quinonoid representation largely on the argument of colours. Wolff's formulae received some support in 1912 from a comparative study by Lifschitz[4] of the absorption spectra of some diazo-oxides and diazo-acetic ester.

In books published in the late thirties the structure of these compounds was put forward as quinonoidal by Sidgwick[5] and as cyclic by Heilborn[6] and Saunders[7]. In 1943 Hodgson and Marsden[8] postulated quinonoid forms where possible and ionic structures where the former are not feasible, and also suggested that all known diazo-oxides can be best regarded as resonance hybrids of the type



A comparison of the visible and ultra violet spectra of diazo-oxides and their corresponding quinones was carried out in 1945 by Anderson and Roedell[9] who arrived at the conclusion that the diazo-oxides were structurally related to the quinones.

From a study of the displacement moment and spectra of a number of ortho and para-diazo-oxides Anderson and Le Fevre and Wilson[10], (1949), helped to rule out completely the possibility of bridged structures even in the case of the ortho diazo-oxides for it was shown by these authors that the dipole moments of these compounds agreed best with the values estimated for quinonoid structures. Furthermore it was shown from purely chemical considerations that they are not bridged, unlike their sulphur analogues.

In 1945 a study of the infrared spectra of some representative compounds in the (N-N) and (C-O) stretching regions was made by Le Fevre, Souza and Werner[11], who concluded from the strong band at 2100 cm^{-1}

that the linkage between the nitrogen atoms was of between double and triple bond type and from the lower frequency of the ($C=O$) stretching mode compared to the corresponding quinones that the carbon-oxygen was modified in the sense ($C\overset{\curvearrowright}{=}O$).

2. Introduction to the Normal Co-ordinate Analysis:

Accounts of a considerable number of proceedures for calculating the vibrational frequencies of molecular systems have been published in the past few years. Some of the more recent publications dealing with molecules containing redundant co-ordinates have tended to retain their redundant co-ordinates throughout the calculation[43]. It is thought that the resulting simplicity, and hence, economy of the computational work are possibly the main reasons for this trend. There is also the fact that by retaining the redundant co-ordinates, one has an in-built check on the correctness of the G-matrix elements. The advent of large computers capable of handling fairly large matrices has made it possible to attack the vibrational problems corresponding to the various symmetry classes collectively; this may be done without any loss of information since it is reasonably easy to find out the symmetries of the various modes by inspection of the eigenvector matrix, L, or Cartesian displacements - see for example table (DO- XVI) for 2,6:dichloro p-benzene-diazo-oxides.

2a The Internal Co-ordinates:

The in-plane and out-of-plane co-ordinates defined for C_6H_6 in Wilson, Decius and Cross[17] were used, in addition to these, there are the (C-N-N) in-plane and out-of-plane bends in the case of diazo-oxides, and the corresponding co-ordinates for NH_2 and OH groups in the amino-phenols and the hydroquinones. β and γ(C-N-N) are defined as the departure from collinearity of the (C-N) bond with the (N-N) bond.

The NH_2 and OH groups were treated as being coplanar with the ring and the in-plane bending co-ordinates defined as changes in the (C-N-H), or (C-O-H) angle and the out-of-plane bending co-ordinates defined as a departure from coplanarity with the carbon skeleton. The in-plane co-ordinates are assigned numbers, 1-2N, this enables one to use a convenient coding system for the diagonal and non-diagonal force constants and G-matrix elements which results in conceptual as well as computational advantages. Force constant f_{ii}, is then denoted $f(n \times 100 + n)$ where n is the number given to the internal co-ordinate; similarly a non-diagonal constant is designated $f(n \times 100 + m)$ where $n \neq m$.

2b The G-matrix:

This is defined by $G = BM^{-1}B$ where M^{-1} is the diagonal matrix of the reciprocal masses and B is defined by $R = B\times$ where x is the Cartesian displacement matrix 3N x 3N and R is our set of internal co-ordinates. The elements of B are computed from Wilson's definition of the displacement vectors associated with various internal co-ordinates (NCA-III). The B-matrix is therefore a square matrix (3N x 3N) with row labels corresponding to the internal co-ordinates in the order shown in fig. 1a, and column labels corresponding to the X, Y and Z components of the displacement vectors acting on the atoms in question. The in-plane and out-of-plane B- and G- matrices are dealt with in separate programmes.

2c The Force Fields:

All the molecules in this study contain the fragment $p\text{-}X^1C_6Y_4X^4$

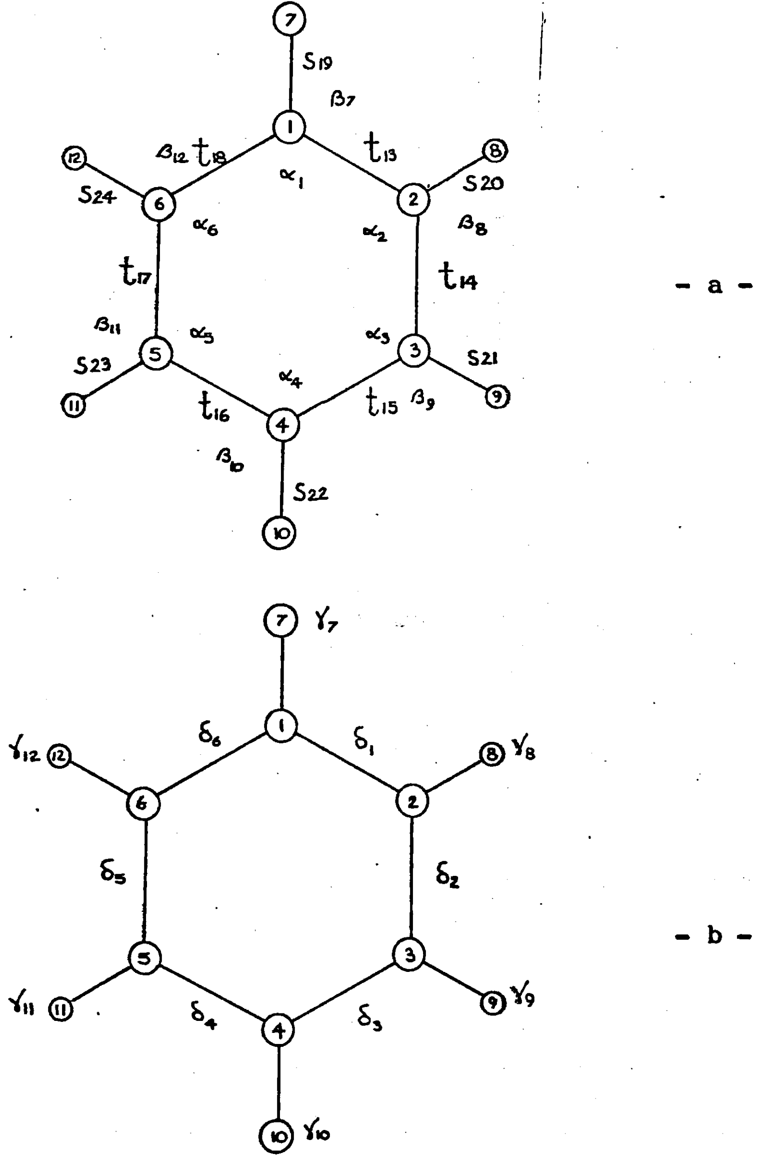

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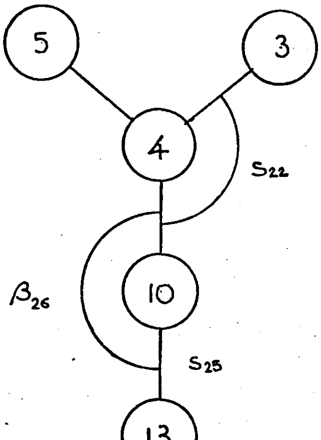
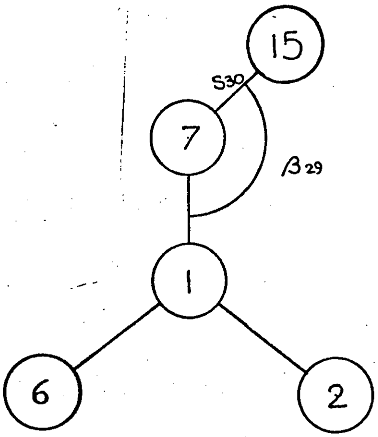
Figure (NCA I)



IIa



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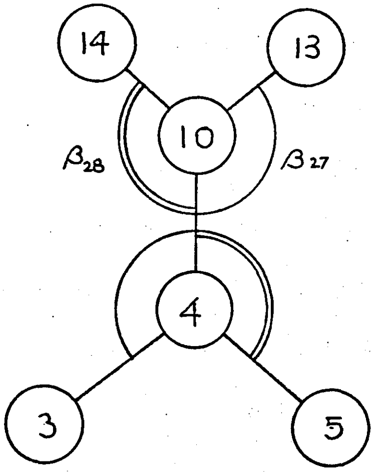


IIc

Figure (NCA II)

where Y = H, Cl. Instead of dealing with each molecule separately an expression for the potential energy of the simplest molecule in the series, parabenzoquinone, is given and the additional terms which arise in the cases of the other molecules are added as required, (Table NCA-I).

2d The Secular Equation:

Having obtained the F and G-matrices it is possible to set up the secular equation in terms of internal co-ordinates I, or symmetry co-ordinates II. Alternatively it is possible to use a specialised set of co-ordinates III, which are chosen in such a way that the secular matrix is symmetric and therefore much easier to handle.

I. The secular equation, in terms of the internal co-ordinates, R, defined above NCA-II is given by the matrix product H = FG since the in- and out-of-plane problems are being dealt with separately H is of order 2N x 2N in the former and N x N in the latter. Both matrices are generally completely unsymmetric and both are singular of ranks 2N - 3 and N - 3 respectively. The roots of these matrices are found by performing a double Q - R iteration on their lower Hessenberg forms[12, 18] for each selected root a corresponding vector of the Hessenberg matrix is obtained by elimination and the latent vector of the original matrix is formed by back substitution. The vectors are then normalised to have unity as their largest element.

II. The secular equation in terms of symmetry co-ordinate, $\mathcal{R}$, is obtained from the partitioned $\mathcal{F}$ and $\mathcal{G}$ which are defined $\mathcal{F}$ = UFU', and $\mathcal{G} = UGU'$, where U is an orthogonal matrix constructed from the normalised coefficients of the equations expressing the symmetry co-ordinates in terms of the internal co-ordinates (e.g. equations 1-24 for 2,6:Dichloro p-benzoquinone and parabenzoquinone (NCA II).

The factors of F and G are picked out and their respective products formed and solved, using the method outlined below, for their eigenroots and eigen-vectors.

III. In this method the G matrix in terms of internal co-ordinates or the factors corresponding to the various symmetry classes of the partitioned $\mathcal{G}$ matrix, is diagonalised. This is equivalent to redefining the co-ordinate system in question in such a way that the resulting G matrix has no cross terms, i.e. $R^* = AR$. The transformation matrix required for carrying out this co-ordinate transformation is the eigen-vector matrix V of the original G matrix. This may be obtained quite simply by solving the G matrix, using a House-Holder method,[12, 18] for obtaining its roots and characteristic vectors (V). On subjecting the F matrix or the appropriate factor of the partitioned $\mathcal{F}$ matrix to the same co-ordinate transformation one obtains F* or $\mathcal{F}_i$

$$F^* = (V^{-1})' F (V^{-1})$$

from this our symmetrised secular equation may be obtained by multiplying on both sides of the R.H.S. by $(G^*)^{\frac{1}{2}}$

$$H^* = (G^*)^{1/2}(V^{-1})'F(V^{-1})(G^*)^{1/2}$$

or $$H^* = W'FW$$

and $$\Lambda = \Psi' H^* \Psi$$

where $$W' = (G^*)^{1/2}(V^{-1})$$

The first of these procedures is used for all the compounds included in this study as a check on the correctness and accuracy of procedure III, which is used extensively for generating the secular equation and the eigen-vector matrix used in the force field refinement process. Procedure II is used where the molecule being dealt with has symmetry higher than C_s.

2e Potential Energy Distribution (PED)

The potential energy of a vibrating system is given by:

$$2V = Q'\Lambda Q$$

from the above treatment we have $\Lambda = (W\Psi)' F (W\Psi)$

hence $2V = Q(W\Psi)' F (W\Psi) Q \qquad 2V = Q'L'FLQ$

The eigen roots of the secular equation can be expressed in terms of the vectors L,

thus: $\lambda_i = \sum_{j,k} L_{ij} L_{ki} F_{jk} = \sum_{j \leq k} (2 - \delta_{jk}) F_{jk} J_{jk}^{i}$

and: $1 = \sum_{j \leq k} (2 - \delta_{jk}) F_{jk} J_{jk} / \lambda_i = \sum_{j \leq k} (PED)_{jk}$

the potential energy distribution is calculated for all force constants every time iteration is carried out during the refinement process. It is stored and output together with other details of the refinement process.

2f Cartesian Displacement Figures (CDF)

The relationship between the specialised set of co-ordinates R and the Cartesian co-ordinates is given by: $x = [M^{-1} BV] R^{\dagger}$. We also have $R^{\dagger} = \Psi Q$, where Q is a set of normal co-ordinates and Ψ is the eigen-vector matrix of the symmetrical secular equation H*, hence $x = [M^{-1} BV\Psi] Q$ the product $M^{-1}BV$ is calculated entirely from geometrical and mass considerations. It is therefore computed and stored for use during the force field refinement process.

2g The Computer Programmes

The computer programmes were written in EXCHLF for London University's Atlas computer. The construction of the B and G matrices for in-plane and out-of-plane vibrations is carried out in two separate programmes. In each case, however, the programme takes the molecular dimensions and atomic masses as input data. In the case of the in-plane problem the components of the X and Y dimensions of the various bond unit vectors e_{ij} are computed from the input data. From these components, using the formulae given for the resultant vectors, (NCA-III), the elements of the B matrix are calculated, coded and arranged in a 2N x 2N matrix. From this and the diagonal matrix of the reciprocal atomic masses the product $G = B'M^{-1}B$ is formed. The G matrix is solved and symmetrised and the roots are examined to ascertain its rank.

From the eigen vectors, the unsymmetrised G matrix and the square root of its diagonal form the matrix W is formed. This is output or stored on magnetic tape for use in the force field refinement calculations. The matrix product $M^{-1}BV'$ is also output for calculating the CDF at various stages of the refinement process. A zero order set of force constants is then read in, the eigen-frequencies of the secular equation are calculated using procedures I and II.

The formation of unit vectors for calculating the B-matrix, in the case of the out-of-plane problem is, ofcourse, unnecessary instead only the magnitudes of these vectors are calculated from the formulae given in (NCA-III), and these are arranged to give the B-matrix for the out-of-plane motion. The remainder of the procedure is identical to that described above for the in-plane programmes.

2h The Force Field Refinement:

The following is a brief account of the method used for "improving" the zero order force field parameters. It is mainly based on the Least Squares process described by Greavnor et al.[44], and also on the methods outlined by Mills[45, 46].

Starting from a set of (r) force constants f^i which gives rise to a set of (s) roots of the secular equation λ^i, $r \geqslant s$;as compared with an experimental set λ^0. A measure of the fit between these two sets is given by

$$\chi^{i-1} = [\lambda^i - \lambda^0]' P [\lambda^i - \lambda^0] \qquad (1)$$

where a square bracket is used to represent a column matrix and a prime indicates the transpose of a matrix. P is a diagonal matrix whose elements are the appropriately chosen weighting factors. Now let changes Δf^i be made in the initial set of force constants to give the new set $f^{i+1} = f^i + \Delta f^i$, then the new fit is given by

$$\chi^i = [\lambda^i + \Delta\lambda - \lambda^0]' P [\lambda^i + \Delta\lambda^i - \lambda^0] \qquad (2)$$

The new set of force constants is an improvement on f^i if $\chi^{i-1} > \chi^i$. The problem is, therefore, to adjust χ^i so that it is a minimum. Expanding (2) we obtain:

$$\chi^i = [\lambda^i - \lambda^\circ]' P \, [\lambda^i - \lambda^\circ] + 2 [\lambda^i - \lambda^\circ]' P \, [\Delta\lambda^i] + [\Delta\lambda^i]' P \, [\Delta\lambda^i] \quad (3)$$

In order to minimise χ^i with respect to Δf^i it is necessary to express χ^i in terms of the Δf^i; this may be done by establishing a relationship between Δf^i and $\Delta\lambda^i$. An explicit relationship is obviously inaccessible in most practical cases, it is possible, however, to express $\Delta\lambda^i$ as a Taylor's series expansion thus:

$$\Delta\lambda_p^i = \sum_m \left(\frac{\partial\lambda}{\partial f_m^i}\right) \Delta f_m^i + \tfrac{1}{2} \sum_m \sum_{m'} \left(\frac{\partial^2 \lambda_p^i}{\partial f_m^i \partial f_{m'}^i}\right) \Delta f_m^i \Delta f_{m'}^i \quad (4)$$

$(\partial\lambda_p^i / \partial f_m^i)$ is taken to represent the partial derivative of the p^{th} root p with respect to the force constant f_m at the point (i) of the refinement process. If the first term only is considered then the relationship between a set of s values of $\Delta\lambda^i$ and r values of Δf^i is represented in matrix form as;

$$[\Delta\lambda^i] = J^i [\Delta f^i] \quad (5)$$

where J^i is the Jacobean matrix. The problem is, however, that the second and higher terms in equation (4) can be justifiably neglected only when the corrections Δf^i are very small and this is not always the case. The higher terms, on the other hand, are unobtainable except for extremely simple systems, hence, an expression of the $\Delta\lambda^i$ as a more or less exact function of the Δf_m^i cannot be obtained, at present.

The method used for obtaining the Jacobean matrix in this study is a numerical one, it consists of making small increments 0.01 x 10^5 dyne cm^{-1} in one of the force constants and calculating the resulting changes in the roots of the secular equation, this procedure is repeated at every stage of the refinement in order to compute a new J-matrix for use in the subsequent calculation.

Substitution of equation 5 into 3 gives:

$$\chi_1^i \quad [\lambda^i-\lambda^0]'P[\lambda^i-\lambda^0] + 2[\lambda^i-\lambda^0]'PJ[\Delta f^i]+[\Delta f^i]'J^{i\prime}PJ^i[\Delta f^i] \tag{6}$$

Where the subscript appearing on χ^i indicates that equation (6) is a first order approximation. Differentiating with respect to Δf^i and equating to zero gives:

$$[\lambda^i-\lambda^0]'PJ + [\Delta f^i]'J'PJ = 0 \tag{7}$$

which on rearrangement and transposition yields:

$$[\Delta f^{i}] = -[J'PJ]^{-1} J^{i'} P [\lambda^{i} - \lambda^{0}] \tag{8}$$

For the special case where r = s, J^{i} has an inverse thus:

$$[\Delta f^{i}] = -[J^{i}]^{-1} [\lambda^{i} - \lambda^{0}] \tag{9}$$

In the present work the zeroth order force field is first improved by calculating "corrections" to the diagonal elements. This is followed by a series of iterations aimed at improving the non-diagonal force constants. The resulting frequencies together with the criteria of the degree of the fit and potential energy distribution figures are visually examined at every stage of the calculation. An improved force field f^{i} thus obtained is used in calculating a set of cartesian displacement figures which are inspected and compared with those obtained for related molecules before the refinement process is resumed.

The criteria of the fit between sets of calculated and experimental frequencies which are used in this work are:

1. χ^{i};
2. the averaged difference $\sum|(\nu^{i}-\nu^{0})|/N-3$;
3. the weighted average $\sum[|(\nu^{i}-\nu^{0})|/\nu^{0}]$; and
4. the dispersions.

In a given refinement process, the "best" set of force constants are those for which these parameters are at minimum. The refinement programme takes as input the weighting factors, or the diagonal element of the matrix P described above, the zero order force field parameters and the experimental values of the frequencies. Details of the programmes are given in Appendix I.

Table (NCA-I)

The potential energy expression for p-benzoquinone is given by:

$$2V_{PBQ} = \sum_{i}^{6} \alpha \left(\alpha_i\right)^2 + \sum_{i}^{6} \beta_x \left(\beta_{x_i}\right)^2 + \sum_{i}^{6} t_i \left(t_i\right)^2 +$$

$$\sum_{i}^{6} s_x \left(s_{x_i}\right)^2 + \sum_{i}^{6} \alpha\alpha^{\circ} \left(\alpha_i \alpha_{i+1}\right) + \sum_{i}^{6} \alpha\beta_x^{\circ} \left(\alpha_i \beta_{x_{i+1}}\right) - \sum_{i}^{6} \alpha\beta_x^{\circ} \left(\alpha_i \beta_{x_{i-1}}\right) +$$

$$\sum_{i}^{6} \alpha t \left(\alpha_i t_i\right) + \sum_{i=1,4}^{6} \alpha s_x \left(\alpha_i s_{x_i}\right) + \sum_{i}^{6} \beta_x\beta_x^{\circ} \left(\beta_{x_i} \beta_{x_{i+1}}\right) + \sum_{i}^{6} \beta_x\beta_x^{m} \left(\beta_{x_i} \beta_{x_{i+2}}\right) +$$

$$\sum_{i}^{6} \beta_x\beta_x^{p} \left(\beta_{x_i} \beta_{x_{i+3}}\right) + \sum_{i}^{6} - \beta_x t \left(\beta_{x_i} t_i\right) - \sum_{i}^{6} \beta_x t \left(\beta_{x_i} t_{i-1}\right) + \sum_{i=2,3,4,5}^{6} \beta_x t \left(\beta_{x_i} t_{i+1}\right) +$$

$$\sum_{i}^{6} \beta_x t^{m} \left(\beta_{x_i} t_{i+1}\right) + \sum_{i=3,6} \beta_x s_Y^{\circ} \left(\beta_{x_i} s_{Y_{i-1}}\right) - \sum_{i=2,5} \beta_x^{\circ} s_Y \left(\beta_{x_i} s_{Y_{i+1}}\right) - \sum_{i}^{6} \beta_x s_Y^{m} \left(\beta_{x_i} s_{Y_{i-2}}\right) -$$

$$\sum_{i}^{6} \beta s_Y^{m} \left(\beta_x s_{Y_{i+2}}\right) + \sum_{i}^{6} t^{\circ} \left(t_i t_{i+1}\right) + \sum_{i=1,4} t^{m} \left(t_i t_{i+2}\right) + \sum_{i=1,4} t^{p} \left(t_i t_{i+3}\right) +$$

$$\sum_{i=2,5} t^{m'} \left(t_i t_{i+4}\right) + \sum_{i=2,5} t_i^{m'} \left(t_i t_{i+2}\right) + \sum_{i=1,4} t^{\circ} \left(t_i t_{i-1}\right) + \quad t^{p'} \left(t_2 t_5\right) +$$

$$\sum_{i=2,5} \left[\left(t_i s_{Y_{i+2}}\right) + \left(l_i s_{Y_{i-1}}\right)\right] t s_Y^{m} + \sum_{i=2,5} s^{\circ} \left(s_{x_i} s_{x_{i+1}}\right) + \sum_{i=2,5} s^{m} \left(s_{x_i} s_{x_{i+2}}\right) +$$

$$\sum_{i=2,3} s^{p} \left(s_{x_i} s_{x_{i+3}}\right)$$

The expression for the potential energy of p-benzenediazo-oxide has in addition the diagonal and non-diagonal terms arising from the fragment (C-N-N), thus :

$$2V_{DO} = 2V_{PBQ} + s\left(s_{NN}\right)^2 + \beta'\left(\beta_{NN}\right) + \sum_{i=2,6} t s' \left(t_i s_{NN}\right) +$$

$$\sum_{i=3,4} t^{\circ} s' \left(t_i s_{NN}\right) + \sum_{i=1,6} t^{p} s' \left(t_i s_{NN}\right) + \sum_{i=2,6} \beta s' \left(\beta_{x_i} s_{NN}\right) + \sum_{i=3,5} \beta_x s' \left(\beta_{x_i} s_{NN}\right) +$$

$$s_x s' \left(s_4 s_{NN}\right) + \alpha s' \left(\alpha_4 s_{NN}\right) + \sum_{i=2,6} \alpha\beta'^{m} \left(\alpha_i \beta_{NN}\right) + \sum_{i=3,4} \alpha\beta'^{\circ} \left(\alpha_i \beta_{NN}\right) +$$

$$\alpha\beta' \left(\alpha_4 \beta_{NN}\right) \quad \sum_{i=1,4} \left(\beta_x \beta'\right)_i \left(\beta_{x_i} \beta_{NN}\right)$$

The expression for p-aminophenol is related to that of p-benzoquinone by the expression:

$$\begin{aligned}
2V_{AP} = {} & 2V_{PBQ} + \sum s_{NH}(s_{NH_i})^2 + s_{OH}(s_{OH})^2 + \sum \beta_{NH}(\beta_{NH_i})^2 + \\
& \beta_{OH}(\beta_{OH})^2 + s'_{NH}(s'_{1NH}\, s_{2NH}) + \sum_{j=1,4}\sum_{i=1,2}(s_x\beta_{NH})_j\,(s_{x_j}\beta_{NH_i}) + \sum_{i=1,2}\alpha\beta_{NH} \\
& (\alpha_4\beta_{NH_i}) + \alpha\beta^{\circ}_{NH}(\alpha_3\beta_{NH_1}+\alpha_5\beta_{NH_2}) + \alpha\beta^{\circ\prime}_{NH}(\alpha_3\beta_{NH_2}+\alpha_5\beta_{NH_1}) + \\
& \alpha\beta^{m}_{NH}(\alpha_2\beta_{NH_1}+\alpha_6\beta_{NH_2}) + \alpha\beta^{m'}_{NH}(\alpha_2\beta_{NH_2}+\alpha_6\beta_{NH_1}) + \beta_Y\beta^{\circ}_{NH}(\beta_{Y_3}\beta_{NH_1}+\beta_{Y_5}\beta_{NH_2}) \\
& + \beta_Y\beta^{\circ\prime}_{NH}(\beta_{Y_3}\beta_{NH_2}+\beta_{Y_5}\beta_{NH_i}) + \beta_Y\beta^{m}_{NH}(\beta_{Y_2}\beta_{NH_1}+\beta_Y\beta_{NH_2}) + \beta_Y\beta^{m'}_{NH}(\beta_{Y_2}\beta_{NH_2}+ \\
& \beta_{Y_6}\beta_{NH_1}) + t\beta^{\circ}_{NH}(t_3\beta_{NH_1}+t_4\beta_{NH_2}) + t\beta^{\circ\prime}_{NH}(t_3\beta_{NH_2}+t_4\beta_{NH_1}) + t\beta^{m}_{NH}(t_2\beta_{NH_1}+ \\
& t_5\beta_{NH_2}) + t\beta^{m'}_{NH}(t_2\beta_{NH_2}+t_5\beta_{NH_1}) + t\beta^{p}_{NH}(t_2\beta_{NH_2}+t_5\beta_{NH_2}) + t\beta^{p'}_{NH}(t_1\beta_{NH_2}+ \\
& t_6\beta_{NH_2}) + \beta'_{NH}(\beta_{NH_1}\beta_{NH_2}) + \sum_{i=2,6}\alpha\beta^{\circ}_{OH}(\alpha_i\beta_{OH}) + \sum_{i=3,5}\alpha\beta^{m}_{OH}(\alpha_i\beta_{OH}) + \\
& \alpha\beta_{OH}(\alpha_1\beta_{OH}) + \sum_{i=2,6}\beta_Y\beta^{\circ}_{OH}(\beta_{Y_i}\beta_{OH}) + \sum_{i=3,5}\beta_Y\beta^{m}_{OH}(\beta_{Y_i}\beta_{OH}) + \sum_{i=1,6}t\beta^{\circ}_{OH} \\
& (t_i\beta_{OH}) + \sum_{i=2,5}t\beta^{m}_{OH}(t_i\beta_{OH}) + \sum_{i=3,4}t\beta^{p}_{OH}(t_i\beta_{OH}) + s_Y\beta_{OH}(s_1\beta_{OH}) + \\
& s_Y\beta^{p}_{OH}(s_Y\beta_{OH})
\end{aligned}$$

For p-hydroquinone we have:

$$\begin{aligned}
2V_{HQ} = {} & 2V_{PBQ} + \alpha\beta_{OH}\sum(\alpha_i\beta_{OH_i}) + \alpha\beta_{OH}\Big[\sum_{i=2,6}(\alpha_i\beta^{1}_{OH}) + \sum_{i=3,5}(\alpha_i\beta^{4}_{OH})\Big] \\
& + \alpha\beta^{m}_{OH}\Big[\sum(\alpha_i\beta^{4}_{OH}) + \sum(\alpha_i\beta^{1}_{OH})\Big] + \beta_Y\beta_{OH}\Big[(\beta_{Y_2}\beta^{1}_{OH}) + (\beta_{Y_5}\beta^{4}_{OH}) - (\beta_{Y_6}\beta^{1}_{OH}) - \\
& (\beta_{Y_3}\beta^{4}_{OH})\Big] + \beta_Y\beta^{m}_{OH}\Big[(\beta_{Y_3}\beta^{1}_{OH}) + (\beta_{Y_6}\beta^{4}_{OH}) - (\beta_{Y_5}\beta^{1}_{OH}) - (\beta_{Y_2}\beta^{4}_{OH})\Big] +
\end{aligned}$$

$$t\beta_{OH}^{o}\,(t_i\beta_{OH}^{1}) + t\beta_{OH}^{o}(t_i\beta_{OH}^{4}) + t\beta_{OH}^{m}\left[(t_i\beta_{OH}^{1}) + (t_i\beta_{OH}^{4})\right] +$$

$$\sum_{i=1,4} s_x\beta_{OH}\,(s_{x_i}\beta_{OH_i}) + \beta_{OH}^{1}\,(\beta_{OH}^{1} + \beta_{OH}^{4}) + s_{OH}\,(s_{OH}^{1} + s_{OH}^{4})$$

Additional terms have to be included when the chlorinated derivatives of the molecules are considered. These terms arise from the necessity of taking into account the interactions of (C-Cl) stretching vibrations with (C-H) and (C-X) stretching and other vibrations. To illustrate this let us consider the 2,6:dichloro p-benzoquinone molecule:

$$2V_{26Q} = 2V_{PBQ} + s_o s_{Cl}^{o}\left[(s_o^{1} s_{Cl}^{2}) + (s_o^{1} s_{Cl}^{6})\right] + s_o s_{Cl}^{m}\left[(s_o^{4} s_{Cl}^{2}) + (s_o^{4} s_{Cl}^{6})\right]$$

$$\beta_H s_{Cl}^{o}\left[(\beta_H^{3} s_{Cl}^{2}) - (\beta_H^{5} s_{Cl}^{6})\right] + \beta_H s_{Cl}^{p}\left[(\beta_H^{3} s_{Cl}^{6}) + (\beta_H^{5} s_{Cl}^{2})\right] + t s_{Cl}^{o}\left[(t^{1} s_{Cl}^{2})\right.$$

$$\left. + (t_2 s_{Cl}^{2}) + (t^{5} s_{Cl}^{6}) + (t^{6} s_{Cl}^{6})\right] + t s_{Cl}^{m}\left[(t^{3} s_{Cl}^{2}) + (t^{6} s_{Cl}^{2}) + (t^{1} s_{Cl}^{6}) + (t^{4} s_{Cl}^{6})\right] +$$

$$t s_{Cl}^{p}\left[(t^{5} s_{Cl}^{2}) + (t^{4} s_{Cl}^{2}) + (t^{2} s_{Cl}^{6}) + (t^{3} s_{Cl}^{6})\right] + \alpha s_{Cl}^{o}\left[(\alpha_2 s_{Cl}^{2}) + (\alpha^{6} s_{Cl}^{6})\right] +$$

$$\alpha s_{Cl}^{o}\left[(\alpha^{1} s_{Cl}^{2}) + (\alpha^{3} s_{Cl}^{2}) + (\alpha^{1} s_{Cl}^{6}) + (\alpha^{5} s_{Cl}^{6})\right]$$

Table (Q-NCA-II)

Symmetry Co-ordinates For Para-benzoquinone.

$$S_1 = (\alpha_1 + \alpha_4)/\sqrt{2}$$

$$S_2 = (\alpha_1 - \alpha_4)/\sqrt{2}$$

$$S_3 = (\alpha_2 + \alpha_3 + \alpha_5 + \alpha_6)/2$$

$$S_4 = (\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)/2$$

$$S_5 = (\alpha_2 - \alpha_3 - \alpha_5 + \alpha_6)/2$$

$$S_6 = (\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)/2$$

$$S_7 = (\beta_1 + \beta_4)/\sqrt{2}$$

$$S_8 = (\beta_1 - \beta_4)/\sqrt{2}$$

$$S_9 = (\beta_2 + \beta_3 + \beta_5 + \beta_6)/2$$

$$S_{10} = (\beta_2 - \beta_3 + \beta_5 - \beta_6)/2$$

$$S_{11} = (\beta_2 - \beta_3 - \beta_5 + \beta_6)/2$$

$$S_{12} = (\beta_2 + \beta_3 - \beta_5 - \beta_6)/2$$

$$S_{13} = (s_1 + s_4)/\sqrt{2}$$

$$S_{14} = (s_1 - s_4)/\sqrt{2}$$

$$S_{15} = (s_2 + s_3 + s_5 + s_6)/2$$

$$S_{16} = (s_2 - s_3 + s_5 - s_6)/2$$

$$S_{17} = (s_2 - s_3 - s_5 + s_6)/2$$

$$S_{18} = (s_2 + s_3 - s_5 - s_6)/2$$

$$S_{19} = (t_2 + t_5)/\sqrt{2}$$

$$S_{20} = (t_2 - t_5)/\sqrt{2}$$

$$S_{21} = (t_1 + t_3 + t_4 + t_6)/2$$

$$S_{22} = (t_1 - t_3 + t_4 - t_6)/2$$

$$S_{23} = (t_1 - t_3 - t_4 + t_6)/2$$

$$S_{24} = (t_1 + t_3 - t_4 - t_6)/2$$

$$S_1 = (\delta_2 + \delta_5)/\sqrt{2}$$

$$S_2 = (\delta_2 - \delta_5)/\sqrt{2}$$

$$S_3 = (\delta_1 + \delta_3 + \delta_4 + \delta_6)/2$$

$$S_4 = (\delta_1 - \delta_3 + \delta_4 - \delta_6)/2$$

$$S_5 = (\delta_1 - \delta_3 - \delta_4 + \delta_6)/2$$

$$S_6 = (\delta_1 + \delta_3 - \delta_4 - \delta_6)/2$$

$$S_7 = (\gamma_1 + \gamma_4)/\sqrt{2}$$

$$S_8 = (\gamma_1 - \gamma_4)/\sqrt{2}$$

$$S_9 = (\gamma_2 + \gamma_3 + \gamma_5 + \gamma_6)/2$$

$$S_{10} = (\gamma_2 - \gamma_3 + \gamma_5 - \gamma_6)/2$$

$$S_{11} = (\gamma_2 - \gamma_3 - \gamma_5 + \gamma_6)/2$$

$$S_{12} = (\gamma_2 + \gamma_3 - \gamma_5 - \gamma_6)/2$$

Definition of Symmetry Co-ordinates for 2,6:dichloroparabenzoquinone

Table (NCA-II) Cont.

In-plane

$S_1 = \alpha_1$

$S_2 = \alpha_4$

$S_3 = (\alpha_2 + \alpha_6)/\sqrt{2}$

$S_4 = (\alpha_3 + \alpha_5)/\sqrt{2}$

$S_5 = (\alpha_2 - \alpha_6)/\sqrt{2}$

$S_6 = (\alpha_3 - \alpha_5)/\sqrt{2}$

$S_7 = \beta_1$

$S_8 = \beta_4$

$S_{10} = (\beta_3 + \beta_5)/\sqrt{2}$

$S_{11} = (\beta_2 + \beta_6)/\sqrt{2}$

$S_{12} = (\beta_2 - \beta_6)/\sqrt{2}$

$S_{13} = (\beta_3 - \beta_5)/\sqrt{2}$

$S_{14} = s_1$

$S_{15} = s_4$

$S_{16} = (s_2 + s_6)/\sqrt{2}$

$S_{17} = (s_3 + s_5)/\sqrt{2}$

$S_{18} = (s_3 - s_5)/\sqrt{2}$

$S_{19} = (s_2 - s_6)/\sqrt{2}$

$S_{20} = (t_1 + t_6)/\sqrt{2}$

$S_{21} = (t_1 - t_6)/\sqrt{2}$

$S_{22} = (t_2 + t_5)/\sqrt{2}$

$S_{23} = (t_3 + t_4)/\sqrt{2}$

$S_{24} = (t_2 - t_5)/\sqrt{2}$

$S_9 = (t_3 - t_4)/\sqrt{2}$

Out-of-plane

$S_1 = (\delta_1 + \delta_6)/\sqrt{2}$

$S_2 = (\delta_2 + \delta_5)/\sqrt{2}$

$S_3 = (\delta_3 + \delta_4)/\sqrt{2}$

$S_4 = (\delta_1 - \delta_6)/\sqrt{2}$

$S_5 = (\delta_2 - \delta_5)/\sqrt{2}$

$S_6 = (\delta_3 - \delta_4)/\sqrt{2}$

$S_7 = \gamma_1$

$S_8 = \gamma_4$

$S_9 = (\gamma_2 + \gamma_6)/\sqrt{2}$

$S_{10} = (\gamma_3 + \gamma_5)/\sqrt{2}$

$S_{11} = (\gamma_2 - \gamma_6)/\sqrt{2}$

$S_{12} = (\gamma_3 - \gamma_5)/\sqrt{2}$

Table (NCA -III)

In-plane Co-ordinates

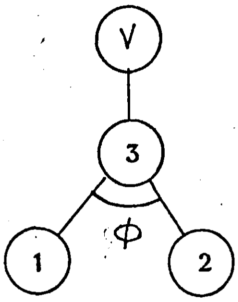
Stretching Co-ord. (t,s)

Displacement vectors $1 = e_1$

$2 = e_2 = -e_1$

Bending Co-ordinates (α)

Displacement vectors



$1 = (\cos\phi\; e_{31} - e_{32})/ r_{31} \sin\phi$

$2 = (\cos\phi\; e_{32} - e_{31})/ r_{32} \sin\phi$

$3 = (r_{31} - r_{32}\cos\phi)\, e_{31} + (r_{32} - r_{31}\cos\phi) e_{32} / r_{31} r_{32} \sin\phi$

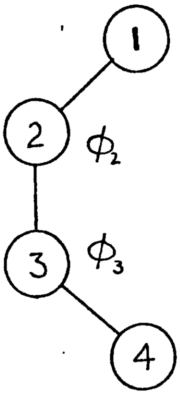
C - V bending Co-ordinates (β_{CV}) $= \frac{1}{2}(\alpha_{n+1} - \alpha_{n+2})$

Table (NCA-III) (Cont.)

Out-of-plane Co-ordinates

Displacement vectors perpendicular to molecular plane (C-C-C-C) torsion (δ).

Displacement vectors.



$1 = -1/\ r_{12}\ \sin\phi_2$

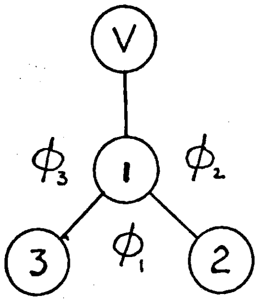
$$2 = -\frac{(r_{23} - r_{12}\cos\phi_2)}{r_{23}\ r_{12}\ \sin\phi_2} + \frac{\cos\phi_3}{r_{23}\ \sin\phi_3}$$

$$3 = -\frac{(r_{23} - r_{34}\cos\phi_3)}{r_{23}\ r_{34}\ \sin\phi_3} + \frac{\cos\phi_2}{r_{23}\ \sin\phi_2}$$

$4 = 1/\ r_{34}\ \sin\phi_3$

(C-V) Bending Co-ordinate (C-V)

Displacement vectors



$V = 1/\ r_{1v}$

$2 = \sin\phi_2\ /\ r_{12}\ \sin\phi_1$

$3 = \sin\phi_3\ /\ _{13}\ \sin\phi_1$

$1 = \div 1/\ r_{1v} - (\sin\phi_2\ /\ r_{12}\ \sin\phi_1) - (\sin\phi_3\ /\ r_{13}\ \sin\phi_1)$

2i Experiments in Force Constant Calculation:

Two additional methods for calculating force constants have been tried, the first is applicable to systems where all types of redundancies have been eliminated, or do not exist.

An initial force field is used in calculating a set of frequencies f^{o}, these are then modified in order to obtain a fractionally better fit with the observed frequencies, and a new secular equation is calculated from the initial eigen vectors V ;

$$\mathcal{H}^{(1)} = (V^{-1}) \Lambda^{(0)} (V^{-1})'$$

from $\mathcal{H}^{(1)}$ the corresponding $F^{(1)}$ matrix is then calculated from $F^{(1)} = W^{(-1)} \mathcal{H}^{(1)} W^{(-1)}$, and the new force constants are used to calculate a second approximation $\Lambda^{(1)}$. A very large number of cycles was found to be necessary to obtain a good fit with the experimental frequencies of ethylene and its chloro derivatives, and even then the results were not always physically meaningful.

In the second method an attempt was made at obtaining convergence by establishing certain, somewhat arbitrary relations between the force constants, this method, although possibly more reliable than the former, results in considerable retardation in the rate of improvement. The main problem here is the arbitrary nature of the relationships set up within the force field. It is probable that this latter method could be used with advantage when the nature, and maybe the approximate form, of the relations between the force constants have been determined from other calculations.

The least squares method has been used to calculate sets of force constants corresponding to hypothetical sets of frequency values for a model system (C_6).

There is as yet no criterion that is universal and well defined for deciding when a given fit between calculated and experimental frequency values is a good one. Califano[57] says, however, that an average deviation from the experiemental values of about 10 or less wavenumbers is acceptable. The average deviation in the case of the above calculation is generally better than 5 cm^{-1}.

A number of factors will influence the agreements between the pairs of calculated and experimental values, of the most imp ortant are :

1. the choice of molecular dimensions;
2. the choice of initial "given" set of force constants; and
3. the values of the experimental frequencies (assignment).

These factors will influence the calculation in general. Other factors which will control or at least influence the speed of convergence in any on cycle of the calculation include numbers 2 and 3 above and also the nature and extent of constraints imposed upon the force field.

2j Molecular Dimensions:

Quinones: The carbon skeletons of p-benzoquinone and its chloro derivatives were assumed to have the molecular dimensions of quinone as found by Trotter[19] and used by Anno[20]. The C-Cl bond length was assumed to be equal to that of chlorobenzene i.e. 1.65 A. The molecular dimensions of chloranil have been studied however and a (C-Cl) bond length of 1.714 A has in fact been found for this molecule as a result of X-ray studies by Shirley et al[21, 22]. The use of this and other structural parameters in the calculation of the normal vibrational frequencies modes of chloranil and the other chloroquinones alters the calculated frequencies only slightly.

Diazo-oxides: The same dimensions were used for these as for their corresponding quinones. The (N-N) bond length was assumed to be equal to 1.1. A.

p-Aminophenol and Hydroquinones: The Carbon rings in these compounds were assumed to be regular hexagons with a (C-C) bond length of 1.39 A the (C-N) and (C-O) were both assumed to be equal to 1.42 A. The (N-H) and (O-H) bond length was assumed to be equal to 1.00 A. X-ray crystallographic studies of p-aminophenol[21], have shown the (C-O), (C-N) and (C-C) bond lengths to be equal to (1.47), (1.59) and (1.38) A respectively.

Trial calculations of the frequencies assuming slightly different dimension from the above have shown that the introduction of any possible error due to substantial departure from the "correct" geometry do not lead to large overall changes in the frequencies, in fact, the average difference ($\nu^i - \nu^o$) does not usually change by more than 1.0 cm^{-1} or 10% of the generally accepted average difference ($\nu^i - \nu^o$)

Chapter II.

Table (Q-I)

Symmetry Properties of the Quinone Molecules

	Symmetry Point Group	Planar Modes	Non-planar Modes
Parabenzoquinone	D_{2h}	$6a_g+5b_{1g}+5b_{2u}+5b_{3u}$	$3b_{3g}+3b_{1u}+b_{2g}+2a_u$
2 Chloro parabenzoquinone	C_s	$21a'$	$9a''$
2,3:Dichloro parabenzoquinone	C_{2v}	$11a_1 + 10b_2$	$4b_1+5a_2$
2,5:Dichloro parabenzoquinone	C_{2h}	$11a_g + 10b_u$	$4b_g+5a_u$
2,6:Dichloro parabenzoquinone	C_{2v}	$11a_1 + 10b_2$	$6b_1+3a_2$
2,3,5,6:Tetra parabenzoquinone	D_{2h}	$6a_g+5b_{1g}+5b_{2u}+5b_{3g}$	$3b_{3g}+3b_{1u}+b_{2g}+2a_u$

The vibrational spectra of parabenzoquinone have been quite extensively studied by a number of authors e.g. Prichard[23], Anno[20] and others[29, 30, 31], and almost all of the ambiguities associated with them have been adequately resolved and well established assignments for this compound have been arrived at mainly through studies of a number of deuterated quinone derivatives[20, 27].

The spectra of 2,5: and 2,6: dichloroparabenzoquinone and 2, 3, 5, 6:tetrachloroparabenzoquinone have also been considered somewhat less extensively, e.g. more limited regions of their vibrational spectra have been studied and no Raman data is available for the tetrachloro derivative.

Neither 2: chloro parabenzoquinone nor the 2,3:dichloro derivative appear to have been considered.

2:Chloroparabenzoquinone

4000-2000:

The only fundamentals expected in the region are the three (C-H) stretches. A weak band is observed in the solid state spectrum at 3056 cm^{-1}, which has a shoulder at 3082 cm^{-1}. The (C-H) stretches are assigned two to the first and one to the second absorption.

2000-1000 cm^{-1}:

The solid state spectrum contains three very intense absorption at 1684, 1660 and 1594 cm^{-1} the second and third have somewhat indefinite shoulder absorptions at 1653, and 1545 cm^{-1}.

The Raman spectrum contains four quite distinct bands in this region at 1684, 1672, 1657 and 1593 cm^{-1}. They are assigned as ν s(C-O), ν s(C-C), ν as(C-O), ν as(C-C) modes respectively. The corresponding infrared assignments are 1684, 1660, 1653 and 1594 cm^{-1} and the respective assignments in the case of p-benzoquinone are 1686, 1667, 1660 and 1592 cm^{-1}. The shoulder band at 1545 cm^{-1} in the infrared spectrum of the solid is quite possibly a combination tone (e.g. 641 + 917 = 1558 cm^{-1}). The bands at 1373 in the infrared and 1374 in the Raman spectra are assigned as a ν(C=C) stretching vibration, there is a corresponding vibration at 1357 cm^{-1} in the spectrum of benzoquinone. The relatively weak band occuring at 1323 cm^{-1} in the Raman spectrum probably corresponds to the strong absorption at 1324 cm^{-1} in the infrared spectrum and it is assigned to a β(C-H) bending motion. All absorptions in this region are expected to have a fair share of ν (C-C), ν(C=C) and β(C-H) motion. Two weak bands occur at 1290 and 1276 cm^{-1} in the Raman spectrum, these correspond to the very strong band at 1286 cm^{-1} which has an unresolved shoulder inflexion at 1266 cm^{-1} in the infrared spectrum of the solid and $CHBr_3$ solution. The main absorption is assigned to a (C-C) stretching vibration while the shoulder absorption which occurs in both the solid and solution is probably associated with a combination tone (e.g. 847 + 434 = 1281; 641 + 604 = 1245). The Raman spectrum contains a strong band at 1204 cm^{-1} with an extremely weak shoulder at 1220 cm^{-1}. The infrared spectrum of the $CHBr_3$ solution contains a medium-intensity band at 1207 cm^{-1} and the solid state spectrum has a weak-medium intensity absorption at 1203 cm^{-1} and an extremely weak absorption is observed at 1215 cm^{-1} in the solid spectrum only. The absorption at 1207 cm^{-1} in the Raman and 1203 cm^{-1} in the infrared is assigned to another (C-C) stretching mode and the weak absorption at 1215 cm^{-1} in the solid spectra is assigned as a possible combination band (e.g. 641 + 564 = 1205 or overtone 604 x 2 = 1208 cm^{-1}). The second β(C-H) bending frequency gives rise to a moderately intense band in the Raman and infrared at 1110 and 1096 cm^{-1} respectively and the third band to an absorption at 1027 cm^{-1}. The only assignment left in this region is the (C-Cl) stretching mode. This is assigned to the intense absorption at 1004 cm^{-1} in the solid and solution spectra. This band contains an intense but not very well defined shoulder absorption at 996 cm^{-1} in the solid state spectrum which could be assigned as a (C-H) out-of-plane banding mode. However, in the spectrum of the CCl_4 solution shoulder absorption seems to disappear completely, this may be due to the fact that the CCl_4 solution is less concentrated and the shoulder absorption is consequently more difficult to see. The Raman spectrum however, contains a weak absorption at 994 cm^{-1} with a resolved shoulder band at 1004 cm^{-1}. An alternative assignment to this shoulder band is a combination band. (e.g. 434 + 564 = 998 cm^{-1}). An assignment has been made for the highest out-of-plane (C-H) bending vibration in the case of p-benzoquinone which puts this mode at 998 cm^{-1}.[20].

Region 400-40:

The shoulder band at 994 cm^{-1} in the Raman and 996 cm^{-1} in the infrared spectra is provisionally assigned as a γ(C-H) out-of-plane deformation and so are the intense bands at 913 and 834 cm^{-1} in the infrared spectrum of the solid phase.

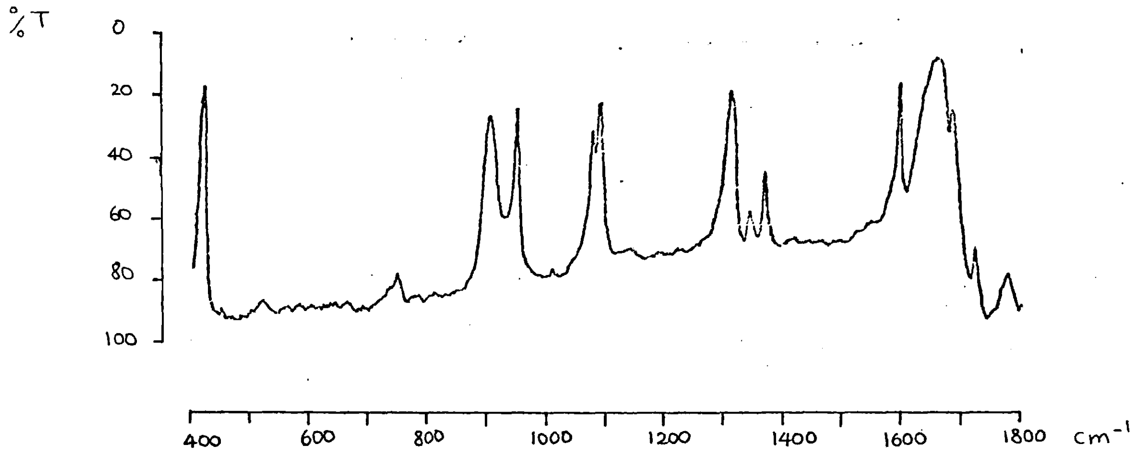
The absorption at 847 cm^{-1} in the infrared spectrum of the mull is assigned to ν(C-C) stretching mode and the weak band at 785 cm^{-1} in the infrared and 777 cm^{-1} in the Raman to an in-plane (C-C-C) bend. The relatively intense absorption at 641 cm^{-1} in the spectrum of the solid and the weak one at 604 cm^{-1} are assigned as out-of-plane (C-C) deformations and the ones at 564 and 465 cm^{-1} as in-plane (C-C-C) bends. The only remaining in-plane vibrations in this spectrum are two β(C-O) and one β(C-Cl) bend. They are assigned to the absorptions 432, 352 and 271 cm^{-1}. In the Raman spectrum the band at 365 cm^{-1} becomes far more intense than that at 432 cm^{-1} which is the reverse of the situation in the infrared spectrum. In addition to this, an exceedingly weak line appears at 652 cm^{-1} which cannot be found in the infrared spectrum, this is possibly a combination tone (e.g. $373 + 271 = 644$ cm^{-1}; $80 + 556 = 646$ cm^{-1}). The remaining modes are the third ϕ(C-C) out-of-plane deformation two γ(C-O) and γ(C-Cl) bends. These are assigned to the bands at 372, 271, 180 and 80 cm^{-1}.

Table (Q-II)

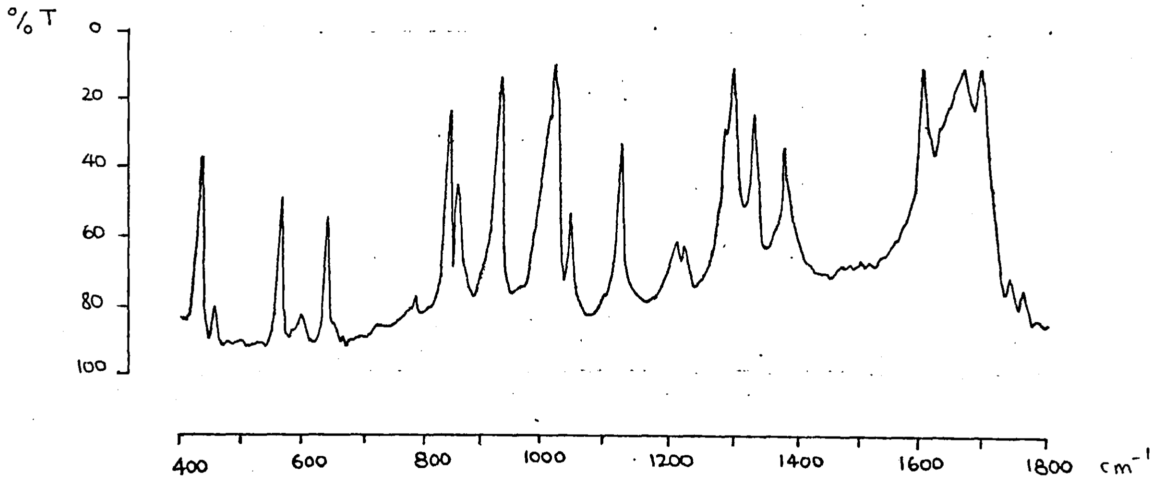
Observed Spectra of 2:Chloro parabenzoquinone

Solid		CHBr$_3$		CCl$_4$		Raman
a	I	a	I	a	I	a
3082	(0.5)					
3056	(1.6)					
1684	(83)	1681	(45)	1684	(82)	1684 (m)
1660	(82)	1661	(90)	1662	(79)	1672 (s)
1653	(30)sh	1632	(35)sh			1657 (ws)
1594	(80)	1590	(88)	1592	(65)	1593 (m)
1545	(30)	1551	(27)	1558	(35)	
1373	(27)	1369	(20)	1368	(8)	1374 (m)
1324	(46)	1313	(74)	1312	(42)	1323 (wm)
1286	(63)	1286	(85)	1283	(64)	1290 (w)
1278	(45)	1266	(50)sh	1270	(35)	1276 (w)
1215	(10)	1207	(36)	1218	(4)	1220 (w)sh
1203	(14)					1204 (s)
1110	(50)	1101	(53)	1096	(35)	1110 (ms)
1032	(30)	1027	(64)			
1004	(75)	1006	(90)	1004	(82)	
996	(50)	992	(25)			994 (vw)
913	(70)	903	(89)	902	(65)	
852	(12)	852	(12)	852	(11)	
847	(37)	847	(26)	844	(22)	
834	(60)	827	(68)	827	(57)	
785	(10)					777 (w)
641	(38)	-		638	(22)	
604	(10)	602	(26)			641 (m)
564	(44)	552	(40)	560	(27)	652 (vw)
465	(13)	463	(10)	460	(50)	600 (vw)
432	(56)	434	(70)	432	(40)	566 (mw)
						459 (vs)
						432 (m)
						373 (vw)
						352 (vw)
						271 (mw)
						241 (ms)
						81 (m)

a cm^{-1} I relative intensities



Infrared spectrum of parabenzoquinone (mull).



Infrared spectrum of 2:chloroparabenzoquinone (mull).

2,3: Dichloro p-benzoquinone:

4000-2000 cm^{-1}:

A single weak-medium absorption occurs at 3080 cm^{-1} in the spectrum of the solid mull. This is readily assigned to the stretching vibrations.

2000-1000:

The solid state spectrum contains a large band with a maximum at 1676 cm^{-1} and shoulder absorptions at 1640 and 1627 cm^{-1}, the solution spectra however have an extremely intense absorption at 1690 cm^{-1} with another relatively weak one at 1622 cm^{-1}. The highest absorption at 1676 cm^{-1} is assigned to the symmetric (C-O) stretching motion and a (C=C)motion, while the lower shoulder band in the solid state spectrum is attributed to the unsymmetric (C-O) stretch. All these absorptions are nevertheless expected to contain significant amounts of (C-O), (C-C) and (C=C), stretching motion in varying degrees of importance. The band occuring at 1569 cm^{-1} in the solid state and solution is readily assigned to a (C-C) stretching vibration. The ill-defined shoulder absorption which appears to be associated with this band could not be resolved. The next band downwards in the spectrum is the weak absorption at 1364 cm^{-1} in the solid and 1370 cm^{-1} in the solution spectrum. This is assigned to a symmetric (C-H) bending mode, although it probably contains a considerable amount of (C-C) stretching motion.

The strong absorption at 1294 cm^{-1} in both the solid and solution spectra is assigned to the unsymmetric (C=C) vibration and the one at

1274 cm^{-1} in the solid state spectrum and 1270 cm^{-1} in the CCl_4 solution spectrum to an unsymmetric (C-H) vibration. This absorption is too weak in the Raman spectrum for its frequency to be ascertained.

The shift at 1292 cm^{-1} in the Raman effect is observed although it is much less intense than its infrared counterpart. The band at 1250 cm^{-1} in both solid and solution spectra is assigned to another symmetric (C-C) stretch which is probably associated with a substantial amount of (C-H) bending as well. The corresponding Raman shift is very intense. Another (C-C) stretching mode probably gives rise to the absorption at 1110 cm^{-1}. The last band in this region occurs at 1036 cm^{-1}, it is assigned to a symmetric (C-Cl) stretch.

1000-400 cm^{-1}:

The intense absorption at 932 cm^{-1} in the solid state is assigned to the unsymmetric (C-Cl) stretch. The Raman spectrum exhibits an extremely weak line in that position but has a moderately weak intensity line at 994 cm^{-1} which is assigned to an out-of-plane (C-H) bend. An intense band occurs at 848 cm^{-1} in the infrared spectra which corresponds to a series of very weak absorptions in the Raman spectrum, this is assigned to the second, possibly antisymmetric, (C-H) deformation.

The absorption at 785 cm^{-1} is assigned to the ring breathing mode, this gives rise to a medium-weak band in the Raman spectrum,and the band at 702 cm^{-1} to an in-plane (C-C) bend. Two bands occur at 558 and 532 cm^{-1} in the infrared spectra which possibly involve bending motion of the ring. In the Raman spectrum, however a series of lines with maxima at 582, 558, 532 and 504 cm^{-1} are observed.

Other modes which occur in this region are assigned in the manner shown in table (Q-VII). The medium-weak absorption at 456 cm^{-1} in the spectrum of the solid appears as a weak band in the solution spectra. However, an extremely strong line is observed in the Raman spectrum at 458 cm^{-1}. This is allocated to a (C-O) in-plane bending, a weak line appears at 468 cm^{-1} in the Raman spectrum, this is possibly a combination tone (e.g. 214 + 263 = 477 cm^{-1}) or a substitute for the assignment of one of the (C-C) deformations.

400-40 cm^{-1}

This region contains two medium intensity shifts at 362 and 352 cm^{-1}, two very intense shifts at 263, 214 cm^{-1} and other weaker ones at 52, 64, 82 and 90 cm^{-1} in addition to an indefinite shoulder inflexion at 120 cm^{-1} and two weak shifts at 180 and 280 cm^{-1}. The first two are assigned as in-plane (C-C-C) and (C-O) deformations respectively. The strong line at 263 cm^{-1} and the infrared band at 120 cm^{-1} are assigned as out-of-plane (C-O) deformations and the lines at 214, 134, 90 and 82 cm^{-1} as in-plane and out-of-plane (C-Cl) bends respectively.

Table (Q-III)

Observed Spectra of 2,3:Dichloro parabenzoquinone

Solid		$CHBr_3$		CCl_4		Raman
a	I	a	I	a	I	
3068	(9)					
1684	(85)	1686	(86)	1690	(78)	1678 (vvs)
1676	(90)	1663	(25)	1686	(70)	1644 (vw)
1627	(40)	1622	(10)	1622	(5)	1619 (m)
1569	(70)	1576	(62)	1565	(60)	1604 (vvw)
1560	(41)	1561	(38)	1557	(35)	1582 (vs)
1364	(18)					1343 (m)
1294	(68)	1293	(55)	1290	(34)	1321 (vvw)
1294	(52)	1274	(28)	1260	(26)	1292 (vvw)
1250	(70)	1252	(37)	1250	(47)	1254 (ms)
1110	(52)	1106	(41)	1104	(29)	1196 (vvw)
1050	(78)	1050	(81)	1050	(60)	1109 (vs)
1036	(50)					994 (vvw)
932	(72)	926	(56)	924	(42)	858 (ww)
785						785 (m)
848	(81)	842	(71)	843	(57)	702 (mw)
702						652 (vvw)
558	(50)	555	(32)	554	(25)	582 (m)
532	(37)			528	(9)	558 (ms)
456	(20)	455	(10)			532 (m)
						504 (m)
						468 (m)sh
						454 (vs)
						362 (m)
						354 (m)
						263 (vs)
						214 (vs)
						82 (ms)

Far Infrared

354 (wb)

263 (m)

235 (ms)

214 (w)

134 (s)b

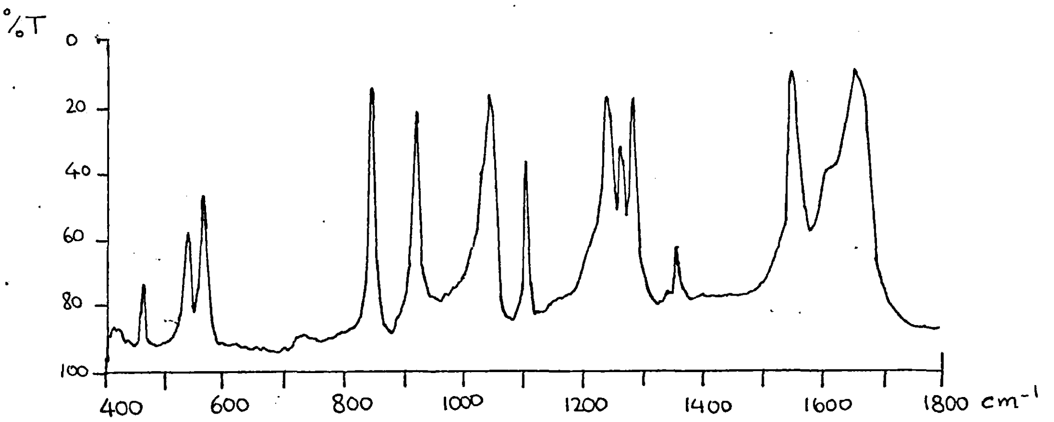
120 (vvs)b

61 (w)sh

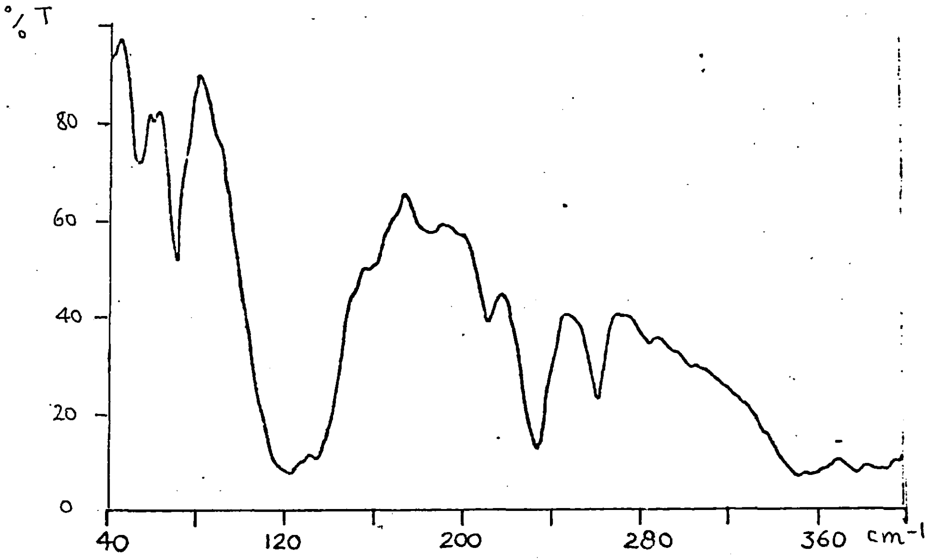
54 (w)

a cm^{-1}

I relative intensity



Infrared spectrum of 2,3:Dichloro parabenzoquinone (mull).



Far infrared spectrum of 2,3:Dichloro para-benzoquinone (wax disc).

This spectrum contains instrumental features - see table (Q-III).

2,5:Dichloroparabenzoquinone:

The Raman spectrum of 2,5:Dichlorobenzoquinone in the solid state is listed in table (Q- IV).

Only nine out of the fifteen Raman active fundamentals have so far been reported. The lines which have been allocated, in the following assignment to fundamental vibrations are marked with an asterisk.

There are in all 18 lines in this spectrum some of which originate from infrared active modes and appear as very weak absorptions. Similarly some of the Raman active fundamentals seem to give rise to exceedingly weak infrared absorptions. It can therefore be said that the selection rules for these centrosymmetric molecules are not very rigidly observed in the solid phase.

2000-1000 cm^{-1}:

The assignments found for this region in the light of the more complete Raman data are in relatively good agreement with those produced by Prichard.

A (C-Cl) stretching and β(C-H) bending mode both having symmetry b_u are assigned to the strong infrared absorption previously observed at 1025 cm^{-1}: The remaining (C-Cl) and (C-H)a_g modes are allocated to the absorptions at 1321 and 1063 cm^{-1}. The latter absorption is not reported by Prichard to have been observed in the Raman spectra of the solutions but is observed by them as a weak band in the infrared spectrum of the solid state. This band is found as a very weak absorption in the spectra which we have recorded using some thick Nujol mulls, but it is not observed in the Raman spectrum of the solid even under conditions of high sensitivity.

It is therefore possible that the assignments of these fundamentals are in error. The only alternative, above 1000 cm^{-1}, for the symmetric ν(C-Cl) assignment is the intense Raman sine at 1195 cm^{-1}, this is probably too high and has already been assigned to a symmetric ν(C-C) stretch. Another possibility is either of the two Raman lines at 885 or 948 cm^{-1}. However it is found from the NCA, that both the high absorption at 1195 cm^{-1} and the one below 1000 cm^{-1} contain a considerable amount of (C-Cl) stretching vibration together with (C-C) stretching and in the case of the lower mode α(C-C-C) bending character. The Raman and infrared frequencies of the spectra recorded for this work in the solid differ to some extent from those reported earlier, the previous values of the frequencies are used in the table showing the assignments of the fundamental vibrations of the chloroquinones, in order to facilitate comparison with earlier work.

1000 - 400 cm^{-1}:

Out-of-plane bending vibrations are expected to give rise to Raman and infrared bands in this region. The symmetric b_g mode is assigned by Prichard[26] to a Raman line at 990 cm^{-1}. This was not listed as observed in the Raman spectrum because of intense excitation source emission in this region, but was observed in the infrared as an exceedingly weak, and unresolved, shoulder band. The Raman spectrum recorded for the present study, using a Ne/He laser source, does not contain a line around the above-mentioned frequency, and the only peaks found in the region 800-1000 cm^{-1} are the ones at 885 and 948 cm^{-1}. The low-intensity line at 948 cm^{-1} is assigned to the symmetric γ(C-H) bending mode and the one at 885 cm^{-1} to the symmetric ν(C-Cl) vibration. The infrared absorption at 905 cm^{-1} which is completely absent from the Raman spectrum is assigned to the a_u (C-H) out-of-plane bending mode.

The Raman lines at 760, 650, 597 and 466 cm^{-1} and the infrared bands at 805, 693 and 602 cm^{-1} remain to be assigned. The vibrational modes expected in this region are the ring breathing mode, in-plane and out-of-plane (C-C) bends and (C-O) in-plane deformation. The latter is assigned to the intense Raman line at 466 cm^{-1} in agreement with the previous assignment by Prichard[26].

The infrared absorption at 805 cm^{-1} does not appear to have been assigned as a fundamental or to a specific combination tone, since the data from the lower regions in the infrared spectrum were not available. Combinations of low frequency infrared and Raman active fundamentals could be produced which would fit this frequency. It still seems that this band is possibly better assigned as a fundamental vibration on account of its strong intensity. A possibble assignment for the 805 cm^{-1} absorption is to the highest α(C-C-C) bending mode, that would give this deformation vibration a higher frequency than the Raman fundamental at 760 cm^{-1} which is best assigned to the ring breathing mode. Alternatively one may have to assume that the infrared absorption at 805 cm^{-1} and the Raman line at 760 cm^{-1} are due to the same vibrational mode, which is rather unlikely since the Raman active lines appear as extremely weak absorptions in the infrared.

Another possibility for the infrared absorption at 805 cm^{-1} is an assignment as an a_u(C-H) bend, this would, however, mean that the earlier assignment of this mode to the absorption at 905 cm^{-1} was in error. The allocation of this absorption to an in-plane (C-H) bend is the only possible alternative, this would at the same time relieve the absorption at 1025 cm^{-1} from its double assignment as a (C-Cl) stretch and a (C-H) bending absorption.

The value of 905 cm^{-1} for an in-plane mode is, nevertheless, lower than the usually expected range, this being beyond or just below 1000 cm^{-1}. For the time being, therefore, it would seem that the best course is to retain the assignment of the infrared band at 805 cm^{-1} as a combination band. It is proposed that a study of the deuterated compound might resolve this difficulty.

The infrared active (C-C) bending mode is assigned to the weak-medium band at 693 cm^{-1} and the remaining infrared absorption at 602 cm^{-1} is allocated to the a_u (C-C) deformation. The Raman absorptions at 650 and 597 cm^{-1} are assigned to the a_g and b_g (C-C) deformations respectively.

400-40 cm^{-1}:

This region is expected to contain absorptions due to the b_u (C-O) bend to a b_g, a_u (C-C) deformation and to out-of-plane (C-Cl) and (C-O) bending modes.

The (C-O) deformations in the case of p-benzoquinone occur at 478 and 408 cm^{-1}. The latter corresponds to the b_u mode in the case of this compound. The only bands observed in the region 200-400 are the weak absorptions at 380, 346, 250 and 224 cm^{-1}. The far infrared spectra do not appear to be very reliable in this region but the γ(C-O) bending mode is, nevertheless, tentatively assigned to the absorption at 380 cm^{-1}. The strong Raman absorption at 370 cm^{-1} is then assigned to the a_g (C-C) bend and the infrared band at 346 cm^{-1} to the remaining a_u (C-C) deformation.

The vibrations left to be assigned in this region are shown in table (Q- VII) together with their possible assignments.

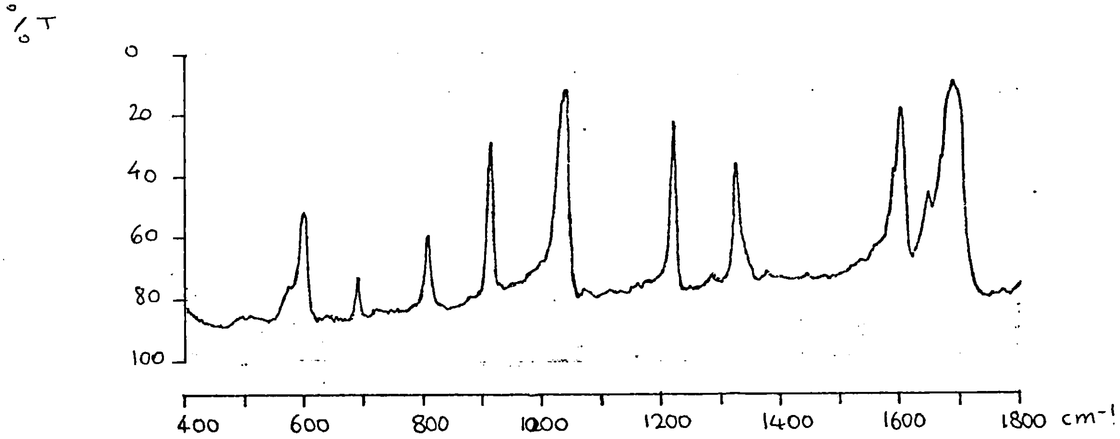
Table (Q-IV)

Observed Spectra of 2,5:Dichloroparabenzoquinone

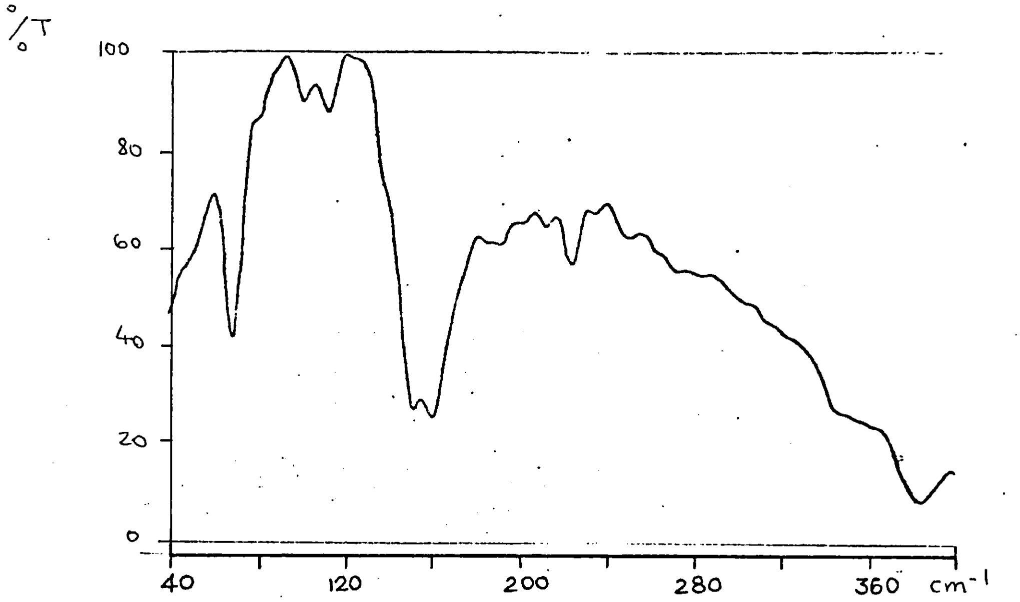
IR (N.J.)		Solution		Raman (Solid)
		CCl_4	$CHBr_3$	
*	Ɨ			*
1674	(70)	1682 (82)	1682 (87)	1668 (vs)*
1652	(45)sh	1620 (9)	1620 (10)	1619 (vs)*
1632	(35)	1584 (70)	1584 (69)	1598 (w)
1588	(51)	1307 (43)	1308 (38)	1321 (ms)*
1575	(31)	1203 (59)	1206 (56)	1299 (w)
1328	(13)sh	1025 (81)	1025 (85)	1195 (s)*
1317	(8)	899 (58)	899 (60)	948 (w)
1278	(4)	794^{**}(16)	796(19)	885 (mw)*
1212	(55)	690 (8)		760 (w)
1063	(4)?	601^{***}(40)	602(44)	650(s)*
1020	(68)			597 (sm)
906	(51)			466 (vs)*
803	(24)			370 (ms)
693	(12)			305 (m)
602	(35)			240 (s)*
585	(9)	Far Infrared		197 (m)
		380(w)		89 (m)
		346(vw)		68 (vs)
		250(vw)		
		224(mw)		
		162(vs)		
		152(vs)		
		140(m)		
		114(mw)		
		102(m)		
		53(m)		

**CS_2

***CH_2Cl_2



Infrared spectrum of 2,5:Dichloro parabenzoquinone (mull).



Far infrared spectrum of 2,5:Dichloro parabenzoquinone (wax disc).

This spectrum contains instrumental features - see table (Q-IV)

2,6:Dichloro p-benzoquinone:

The free molecule belongs to the point group C_{2v} all except three a_2 fundamentals should theoretically be observed in the infrared spectrum. The Raman spectrum of this compound has been recorded in a number of solvents by Prichard[26] but not all the infrared active fundamentals are observed in these spectra. Also the far infrared spectrum has become available and the following is a brief revision of the assignments produced by Prichard in the light of the new information.

2000 - 400 cm^{-1}:

Due to the fact that only a limited region of the Raman spectrum was observed earlier a number of multiple assignments were made. The infrared band at 1041 cm^{-1} for instance was assigned to a b_2 (C-H) bend and b_2 (C-Cl) stretch; a similar situation arose in the case of 2,5:dichloro benzoquinone where the absorption at 1025 cm^{-1} was assigned to both a b_u (C-H) bend and (C-Cl) stretch.

The infrared spectrum of the solid contains an intense absorption at 1043 cm^{-1} which has a rather weak shoulder absorption at 1029 cm^{-1}, this does not appear to have been noted previously. The Raman spectrum on the other hand contains one broad and somewhat weak line at 1036 cm^{-1}. The only other absorptions appearing in the infrared spectrum in the 1200-1000 cm^{-1} region are the weak bands at 1150 and 1089 cm^{-1} which have been previously assigned to symmetric (C-C) and (C-Cl) stretches respectively. No line is observed at 1089 cm^{-1} in the Raman spectrum which is what would be expected if this assignment is in fact the correct one. The remaining (C-Cl) stretch is hence best assigned to some absorption outside this region. The best suited absorptions for this purpose are the ones in the range 800 - 950 cm^{-1}. Of these absorptions the ones at 882 cm^{-1} appear as a much weaker absorption in the infrared than in the Raman spectrum and is therefore quite probably due to the infrared "inactive" (C-H) deformation. The strong absorption observed at 917 cm^{-1} is assigned by Prichard[26] to the b_2(C-H) deformation.

The intense band at 799 cm^{-1} is not likely to be due to the other a_2(C-H) deformation. One is left with the choice between this band and the weak absorption at 866 cm^{-1} for assignment as the lower (C-Cl) stretching vibration. It is nevertheless found that the (C-Cl) stretching character is evident in the lowest (C-C) stretching mode at 1150 cm^{-1} as well as the ring breathing and (C-C) bending modes. The ring breathing mode could be assigned to the absorption at 799 cm^{-1} and the highest (C-C) bending mode to the absorption at 784 cm^{-1} both of these frequencies certainly seem somewhat higher than expected for this type of compound. An alternative assignment might be to allocate the low (C-Cl) stretching vibration to the band at 799 cm^{-1}; the medium-intensity shoulder band at 784 cm^{-1} to the ring breathing mode and the weak band at 866 cm^{-1} to a combination or overtone . Another possibility still would be to assign the infrared absorption at 917 cm^{-1} in the solid state spectrum to the (C-Cl) stretching mode , the lower band at 799 cm^{-1} to the infrared-active (C-H) deformation and the ring breathing mode to the absorption at 784 cm^{-1} (infrared); 782 cm^{-1}(Raman). The decision on which of these possibilities is to be adhered to is made towards the end of this section. The vibrational modes expected in the remaining region are (C-C-C) and (C-O) in-plane bending modes.

Two absorptions are observed in the infrared, a weak one at 667 cm^{-1} and a rather strong one at 447 cm^{-1}. The band at 447 cm^{-1} becomes broader in solution and is probably most suitably assigned as a (C-O) bending mode. The Raman shift at 478 is completely absent from the infrared spectrum. This band was previously assigned as another (C-O) in-plane deformation, but it is possibly advisable to allocate it to an infrared-inactive mode.

There are therefore only three definite absorptions in all, which should be assigned to about five vibrational modes. Inorder to get rid of this rather unsatisfactory situations one may either:

1. change the assignments of the higher region, 750-950 cm^{-1} in such a way so as to include at least one of the (C-C-C) deformations;

2. assume that at least four of these deformations fall below 400 cm^{-1};

3. assume multiple assignments of some of these modes; or, finally

4. assume some unusual lack of activity in both the Raman and the infrared spectra of some of these normally moderately or strongly

active vibrations.

400 - 40:

One of the (C-Cl) out-of-plane bending vibrations is expected to be active in the Raman and perhaps weakly active in the infrared. The strong Raman line at 198 cm^{-1} appears as a very weak absorption in the far infrared at 197 cm^{-1} and is assigned to this mode. Another strong shoulder shift at 106 cm^{-1} in the Raman is assigned to the b_2 mode which gives rise to an absorption at 124 cm^{-1} in the far infrared.

The (C-O) out-of-plane vibrations are allocated to the infrared bands at 263 cm^{-1} and 162 cm^{-1} the in-plane (C-Cl) modes are assigned to the 262 cm^{-1} and 180 cm^{-1} Raman lines. The only vibrations left in this region are the remaining (C-O) in-plane bend and in-plane and out-of-plane (C-C) deformations. These are suitably allocated to the bands at 380, 328 and 304 cm^{-1} in the far infrared. Two peaks only are observed in the Raman spectrum in the region 300-400 cm^{-1} but both of these are rather broad bands with possible shoulder absorptions.

To return to the assignments of the absorptions above 400 cm^{-1} it seems that the most suitable course to adopt, in view of the scarcity of suitable absorptions below 400 cm^{-1} for assignment to the remaining two (C-C-C) deformations, is to adhere to the first alternative and assign the intense absorption at 799 cm^{-1} to the ring breathing mode and the remaining bands at 784, 404 and 667 cm^{-1} to two in-plane and out-of-plane bending vibrations.

Table (Q - V)

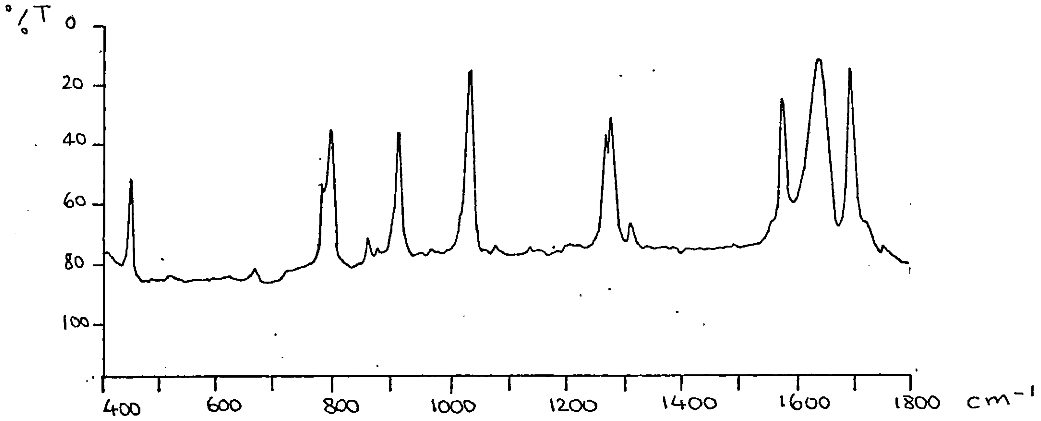
Observed Spectra of 2,6:Dichloroparabenzoquinone

IR (N.J.)		Solution		Raman (Solid)
		CCl_4	$CHBr_3$	
*	I	* I	* I	* I
1705	(60)	1700(52)	1700(64)	1702(vs)
1700	(48)sh	1658(51)	1658(62)	1644(vs)
1655	(73)	1616(12)	1616(14)	1622(m)sh
1581	(54)	1581(47)	1584(59)	1586(vw)
1314	(7)	1314(23)	1315(29)	1330(mw)
1291	(46)	1282(24)	1285(37)	1296(m)
1282	(41)	1271(43)	1271(51)	1283(m)
1150	(3)	1041(50)	1039(80)	1152(vw)
1089	(3)	909(39)	908(63)	1036(vw)
1043	(62)	789^{**}(44)	792(76)	
1029	(15)	779^{**}(36)		
917	(50)			908(w)
882	(3)			880(w)
866	(10)	Far Infrared		800(w)
799	(50)	380(w)		782(w)
784	(30)	304(w)		486(vw)
667	(4)	263(w)		478(m)
447	(32)	192(w)		373(m)
		162(vs)		304(m)
		138(m)		262(m)sh
		124(m)		198(vw)sh
		111(w)sh		180(m)sh
				158(s)sh
				106

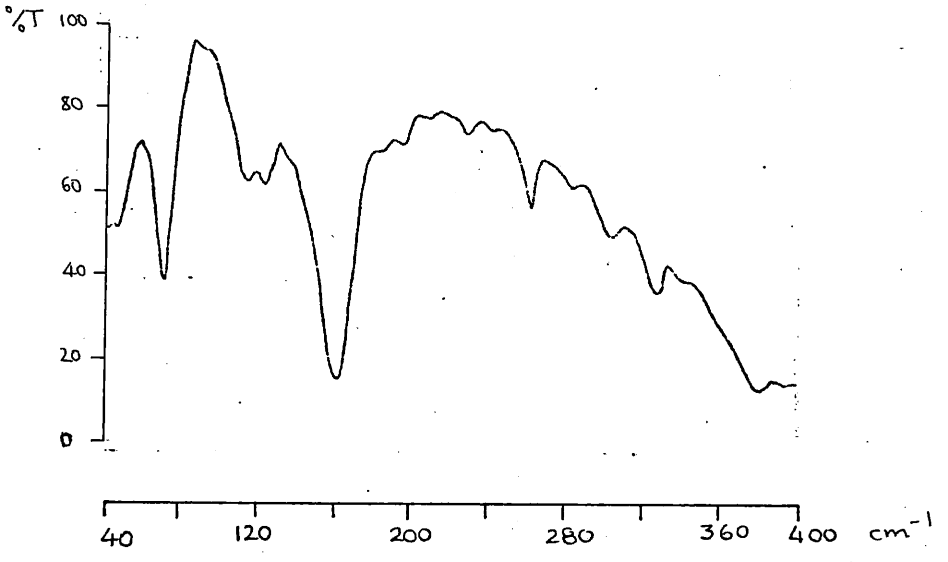
* cm^{-1}

** CS_2 not CCl_4

I relative intensity



Infrared spectrum of 2,6:dichloro parabenzoquinone.



Far infrared spectrum of 2,6:dichloro parabenzoquinone.

The spectrum contains instrumental features – see table (Q-V).

Chloranil:

This molecule is centrosymmetric, and the Raman lines are therefore not expected to be active in the infrared spectrum. The slight non-coplanarity of the molecule and the structure of the unit cell[19] might be expected to relax this selection rule. With certain exceptions, however, this rule is found to hold more or less strictly. Only three coincidences are observed between the Raman and infrared spectra. These occur at 1697, 1262 and 1239 cm^{-1} .

2000-40 cm^{-1}:

The infrared spectrum contains three distinct bands in the region 1500-1700 cm^{-1} they are the medium and weak absorptions at 1574 and 1653 cm^{-1} respectively, and the intense band at 1697 cm^{-1} this latter absorption has a shoulder band at 1701 cm^{-1} and appears to be split.

The Raman spectrum in the same region contains only two intense lines at 1608 and 1690 cm^{-1}, together with a weak shoulder absorption at 1700 cm^{-1} and another exceedingly weak line at 1574 cm^{-1}. The shoulder peak appearing at 1700 cm^{-1} in both the infrared and Raman spectra is probably due to an overtone or a combination band. Four vibrations are expected to give rise to absorptions in this region, they are the two (C-O) stretches b_{1u} and a_g , and two (C-C) stretches b_{2u} and a_g. The first three have been assigned by Prichard[26] to the absorptions at 1697, 1653 and 1574 cm^{-1}. The weak (C-C) mode is assigned to the Raman band at 1608 cm^{-1}. The weak band occuring at 1214 cm^{-1} in the infrared is assigned by Prichard to b_{1g} (C-C) stretch this band is absent from the Raman spectrum and since no other absorptions occur in the region 1010-1240 cm^{-1} this mode is assigned to the absorption at 1246 cm^{-1} which has been allocated by Prichard to another (C-C) b_{2u} stretch. This band appears both in the Raman and the infrared spectra, but it is much weaker in the latter. Another band which appears in both spectra is the one at 1262 cm^{-1} in the infrared, this is considerably weaker in the Raman spectrum and it has been previously assigned to a b_{1u} (C-C) stretch. The remaining b_{2u} (C-C) mode is left to be assigned either to the weak or extremely strong infrared absorption at 1214 and 1119 cm^{-1} respectively. This latter assignment would in fact imply a double assignment at 1119 cm^{-1} since one of the (C-Cl) stretches has to be assigned to this band. (It has been assigned to two such stretches by Prichard and does not occur in the Raman spectrum). The weak band at 1006 cm^{-1} is assigned to an a_g or b_{3g} , (C-C) stretch, another (C-C) mode gives rise to the Raman line observed at 853 cm^{-1}.

The band appearing at 908 cm^{-1} in the infrared spectrum of the solid sample has been allocated to a combination tone by Prichard. If the assignment of only one (C-Cl) stretch to the absorption at 1119 cm^{-1} is accepted then it may be best to assign the remaining b_{1u} or b_{2u} mode to this absorption. The Raman band at 778 cm^{-1} is assigned to the ring breathing mode, this absorption is absent from the infrared spectrum in which two bands are observed at 756 and 716 cm^{-1}. They are assigned to in-plane and out-of-plane deformation vibrations respectively.

Alternative assignments which would preserve the earlier ones made by Prichard are to allocate those two infrared bands to ring breathing and in-plane (C-C) bending modes, this however would mean that the ring breathing mode gives rise to absorptions in both the infrared and Raman spectra at 756 and 778 cm^{-1} respectively. The highest out-of-plane (C-C) deformation is assigned by Prichard to the absorption at 453 cm^{-1} in the CH_2Cl_2 solution. This absorption is not observed in the solid state spectrum at this frequency although an exceedingly weak absorption is found at 474 cm^{-1} in the same spectrum. The strong and medium intensity lines at 494 cm^{-1} and 422 cm^{-1} are inactive in the infrared these may be allocated to the b_{3g} (C-C) or (C-O) bends, the corresponding frequencies for p-benzoquinone, 2,5:dichloro, and 2,6: dichlorobenzoquinone are β(C-O) 487, 472 and 487; and α(C-C-C) 745, 610, ---cm^{-1}. The more intense line at 494 cm^{-1} is therefore assigned to a β(C-O) bend and the one at 422 cm^{-1} to the α(C-C-C) mode. The b_{2u} (C-O) bending vibration is probably best allocated to the band occuring at 374 cm^{-1} in the far infrared spectrum. Two more out-of-plane and one in-plane (C-C) deformations are still to be assigned. The symmetric out-of-plane (C-C) mode is assigned to the shoulder peak associated with the Raman line at 422 cm^{-1}. The rest of these (C-C) deformations probably occur below 400 cm^{-1}. An in-plane mode is allocated to the Raman line at 329 cm^{-1} and out-of-plane vibration to the infrared band at 298 cm^{-1}. The rest of the fundamentals expected in the region below 400 cm^{-1}, comprise in-plane (C-Cl) bends, and out- of- plane

(C-Cl) and (C-O) deformations. Their assignments are shown in table (Q- VII). The assignments were made on the basis of activity in the Raman or the infrared spectra and comparison with the spectra of similar compounds such as the chloroquinones and tetrachlorobenzenes.

Table (Q-VI)

Observed Spectra of Chloranil

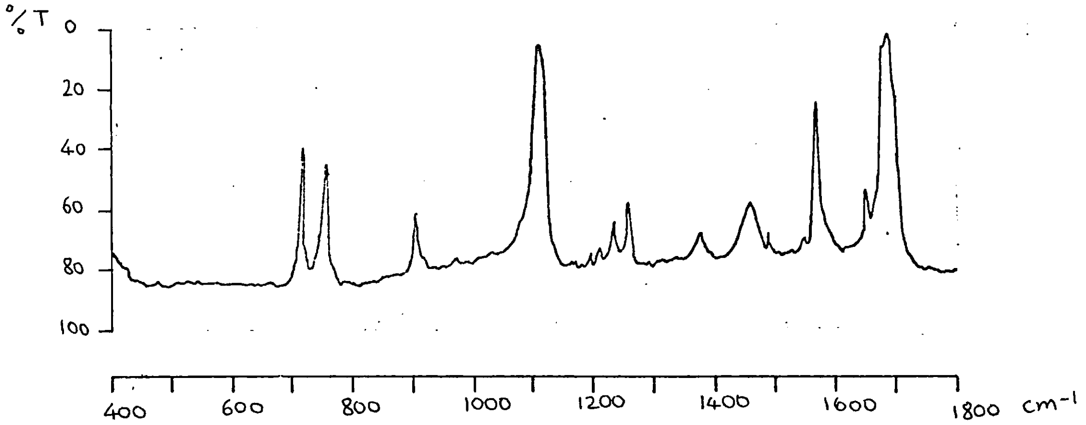
Infrared (Solid)		Raman
*	Ɨ	*
3360	(15)	
1701	(58)sh	1704 (mw) sh
1697	(76)	1690 (vvs)
1684	(73)sh	
1653	(20)sh	
		1608 (vvs)
1574	(50)	1574 (vvw)
1550	(5)	
1493	(51)	
		1284 (mw)
1262	(21)	1266 (m)
1239	(15)	1246 (ms)
1214	(7)	
1198	(4)	
1119	(73)	
1115	(73)^{d}	
		1006 (mw)
908	(18)	
		853 (m)
		778 (m)
756	(40)	
716	(46)	
	(2)	494 (vvs)
	(40) b	422 (m)
474		329 (s)
412		268 (vw)
		197 (s)
		136 (w)sh
		80 (w)sh

Far infrared
Ɨ
376 (vw)?
297 (w)
198 (vs)
177 (vs)
140 (vw)?
96 (m)
80 (m)
60 (m)

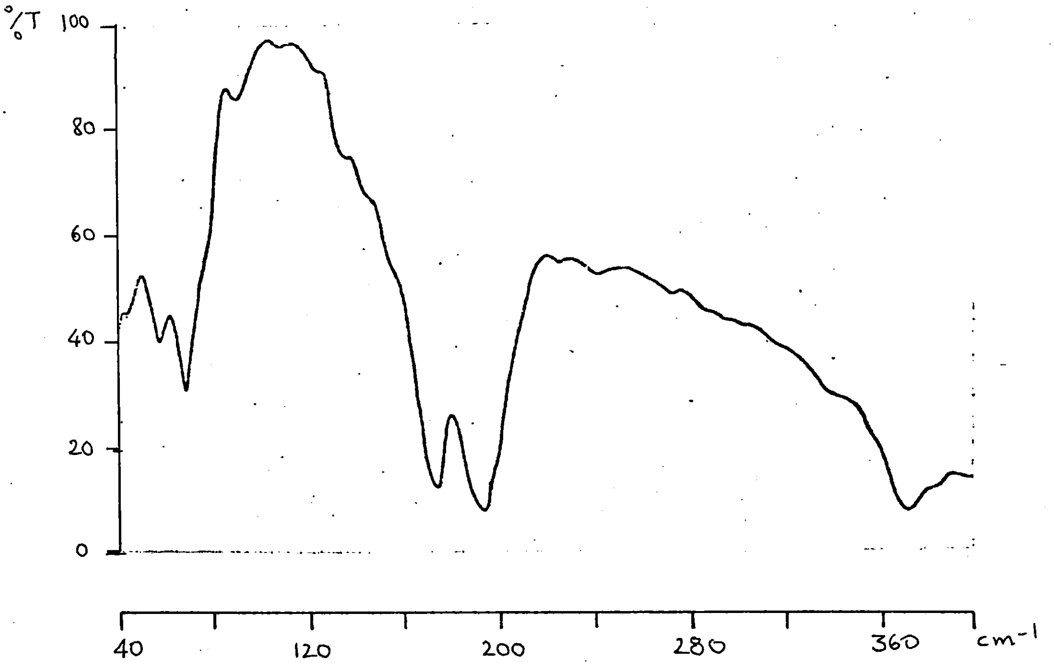
Infrared (CCl_4 Solution)[26]
3359 (vw)
{1695 (vs)**
{1681 (vs)**
1653 (w)***
1560 (s)
1115 (vs)

* cm^{-1}

Ɨ relative intensity



Infrared spectrum of 2,3,5,6:tetrachloro parabenzoquinone (mull)



Far infrared spectrum of 2,3,5,6:tetrachloro parabenzoquinone (wax disc.). This spectrum contains instrumental features - see table (a-VI).

Table (Q-VII)

Assignment of the Vibrational Fundamentals of some Chloro parabenzoquinones

		2Q		23Q	26Q			25Q			2356Q
					*	‡		*	‡		
(C-H)	a'	3082	a_1	3068	3076	3076	b_u	3067	3067		
(C-H)		3056	b_2		3076	3070	a_g	3080	3080		
(C-O)		1684	a_1	1676	1700	1700	a_g	1674	1674	a_g	1653
(C-O)		1653	a_1	1644	1658	1658	b_u	1682	1682	b_{1u}	1097
(C-C)		1660	a_1	1676	1616	1616	a_g	1620	1620	a_g	1608
(C-C)		1594	a_1	1569	1314	1314	a_g	1196	1195	b_{1u}	1574
(C-C)		1203	b_2	1274	1581	1581	b_u	1584	1584	b_{3g}	1246
(C-C)		1286	b_2	1250	1282	1282	b_u	1307	1307	b_{1u}	1262
(C-C)		1373	b_2	1294	1150	1150	b_u	1203	1203	b_{2u}	1214, 1119
(C-H)		1324	a_1	1364	1271	1271	a_g	1321	1321	a_g	1006 ‡
(C-H)		1110	b_2	1110	1041	1041	b_u	1025	1025	b_{3g}	853 ‡
(C-H)		1032									
(C-Cl)		1004	a_1	1036	1083	1041, 1148	a_g	1063	885	b_{1u}	1119
(C-Cl)			b_2	932	1041	882, 917	b_u	1025	1025	b_{2u}	908
RB		847	a_1	785	779	799	a_g	658	760	a_g	778
(C-C-C)		785	a_1	702	487	779	a_g	472	650	a_g	422
(C-C-C)		564	a_1	558	261	304?	a_g	254	370	b_{3g}	329
(C-C-C)		465	b_2	362		323	b_u	601	693	b_{1u}	756
(C-O)		432	b_2	456	443	447	a_g	472	472	b_{3g}	494
(C-O)		352	b_2	352	487	380	b_u		380	b_{2u}	374
(C-Cl)		271	a_1	214	363	263	a_g	254	305	a_g	136
(C-Cl)		-	b_2	180	262	180	b_u		152	b_{3g}	197
(C-Cl)										b_{1u}	244
(C-Cl)										b_{2u}	198

Table (Q-VII) Cont.

		2Q		23Q		26Q			25Q			2356Q
						*	†		*	†		
(C-H)	a"	996	a_2	994	a_2	784	882	b_g	990	948		
(C-H)		913	b_1	848	b_1	905	905, 866	a_u	899	899		
(C-H)		834										
(C-C)		641	a_2	(582)	a_2		487	b_g	602	597	b_{2g}	430
(C-C)		604	b_1	532	b_1	447	667	a_u		602	a_u	298
(C-C)		372	a_2	468, 354	b_1		304	a_u		346	b_{3u}	716
(C-O)		271	a_2	263	b_1		263	b_g		240	b_{2g}	268
(C-O)		180	b_1	120	b_1		124	a_u		162	b_{3u}	197
(C-Cl)		80	a_2	82	a_2	203	106	b_g		197	b_{2g}	308
(C-Cl)			b_1	134	b_1		192	a_u		103	b_{1g}	180
(C-Cl)											a_u	80
(C-Cl)											b_{3u}	148

* Previous assignments

† Present assignments

‡ (C-Cl) not (C-H) vibrations.

Normal Co-rdinate Treatment (Planar Vibrations) :

Tha most recent attempt at calculating a set of force constants for parabenzoquinone was made by Anno[20]. Two trial sets of force constants were calculated. The constants in the first set (set IA table Q-VIII (Å)) are derived from benzene and hexafluorobenzene. Constants involving (C-H) stretching and bending modes and skeletal modes were transferred from benzene[32,33]. For the (C-H) bending/(C-0) stretching interaction constants the corresponding (C-F) bending/(C-F) stretching parameters were used[34]. The constants of the second set (set IIA table VIII (A)) were partly based on the improved first set - except for the diagonal and non-diagonal constants involving the (C-0) and (C-C) stretching motion which were determined from the formula put forward by Coulson and Longuet-Higgins[35]:

$$k_r = (\sigma(1-p_r)+\kappa p_r) + \frac{(1/2)\,\kappa^2\sigma^2(s-\alpha)^2\pi_{r,r}}{(\sigma(1-p_r)+\kappa p_r)^2}$$

where k_r, p_r and $\pi_{r,r}$ are the stretching force constant the bond order and the self-polarisability of the bond r,σ,κ,s and d are the stretching force constant and equilibrium internuclear distance of the single and double bond, respectively.

The first trial force constants of the (C-0) stretching motion was calculated from Badger's formula[36]:

$$r_e = (C/k_e)^{1/2} + d$$

where r_e and k_e are the equilibrium distance and force constant of the bond, respectively and C and d are constants, the numerical values of which are 1.86 and 0.680 respectively, for a bond involving a pair of element in the second row of the periodic table.

The refinement procedure used by Anno consists of allowing the diagonal constants of the trial set of parameters to change until a perfect fit was obtained for a number of calculated parameters - ν_5, ν_{13}, ν_{18}, ν_{21}, see table (VIII-B). The average difference, $\sum(\nu^i - \nu^0)/N$, is smallest for the improved set I, 30.2 cm^{-1}. The corresponding values for the set II are 42.2 and 42.5 cm^{-1} so that although some of the calculated frequencies from improved set II become identical with their experimental values the overall agreement is in no way enhanced. From this one may conclude that set II-A which contains constants calculated using Coulson's formula does not constitute an improvement on set I-A, in the sense that the overall agreement between the calculated and observed frequencies is not improved.

The force field parameters calculated using Coulson's formula are in a number of cases quite different from those for benzenoid type systems reported by Anno themselves and Scherer among other authors. This difference may naturally be accounted for by stating that the bonding systems in p-benzoquinone and benzonoid type molecules are quite different. The inclusion of such parameters instead of benzenoid type parameters would, however, be expected to increase the agreement between the calculated and observed frequencies which is unfortunately not the case. It should also be mentioned that Anno's' NCA report is not accompanied by Cartesian displacement figures this, it is felt, could introduce a potentially dangerous situation when the normal co-ordinates analysis is being relied upon to support one of two alternative assignments, for example.

As in Anno's report the internal co-ordinate used for the (C-C) in-plane bending motion is the same as that defined by Wilson, Decius and Cross[39] i.e. no scaling of the force constants by the bond length was utilised.

The Cartesian Displacement figures which were generated by the method described in section (2f) are reproduced in figures (A-1). Anno's study of the infrared and Raman spectra of parabenzoquinone can justify a considerable degree of certainty in their symmetry assignments of the gas phase spectra, the infrared active bands belonging to symmetry classes b_{2u}, b_{3u} and b_{1u} may be assigned fairly readily according to their characteristic shapes. The arrangement used in their depolarisation measurements is not sufficiently refined to permit accurate quantitative determination of the state of polarisation of the Raman shifts, it is stated however that they were able to identify with certainty depolarisation factors of 0.5 or 0.4 and to identify the strongly polarised bands. This, it is thought, should be born in mind when comparing the results of our normal co-ordinate analyses with their results.

The trial sets I-A and II-A were used independently in the present work as zero approximations from which a number of sets of potential energy parameters were calculated using the refinement methods outlined earlier. Table (Q-VIII-A) contains Anno's sets (I) and (II)[20] together with two of the sets obtained from them (I-B) and (II-B).

The force field proposed by Anno does not distingwish between (C-O) and (C-H) bending interaction parameters with (C-C) stretching , bending and (C-O) stretching and (C-H) bending parameters. This distinction is made in one of the force fields developed in this work. In addition to this non-diagonal terms which take into account interaction between (C-C) bending and (C-H) and (C-O) bending and (C-O) stretching internal co-ordinates in the meta position with respect to one another are introduced.

The (C-C) stretching interaction parameters calculated by Anno differ considerably from those quoted by them for benzene but they are in closer agreement with those found for chlorinated benzenes by Sherer[39].

It may be readily seen that the diagonal constants of the (C-C) stretching motion of set (I-B) is considerably smaller than one might expect, this was found necessary if large off-diagonal parameters, often considerably greater than unity were to be avoided. The value of the (C-C) stretching constant of ethylene is given as 10.8956 and 8.8368 x 10^5 dyne cm^{-1} in earlier literature reports[37]; only the latter value however falls on the curve expressing the relationship between the stretching force constant of a (C-C) bond and the (C-C) bond length.

The (C-C) stretching force constant of benzene and para-substituted benzenes falls in the region $5\text{-}6.5\times10^{-5}$ dyne cm^{-1} and the corresponding value found for ethane[38] is 4.57×10^{-5} dyne cm^{-1}, hence the values of the constants of the (C-C) bond.in parabenzoquinone, (I-B) and (II-B) are probably somewhat low.

The off-diagonal element representing the interaction between (C-C-C) bending and (C-C) stretching - (C-C-C)/(C-C); ortho - has a value of -0.2515 in the force fields used by Anno, sets (I-A) and (II-A). It was found necessary to use a positive value of about 0.3 for this constant in this work, this value is in good agreement with that of the corresponding chlorobenzene force field found by Scherer[39].

The force field parameters listed in table (Q-IXA) were developed from a large number of trial sets of potential energy parameters, which were obtained from the parameters given in table (Q-VIIIA) by introducing small changes in the force constants individually or collectively and then using the least squares refinement process described above to converge upon the experimental set of frequencies. The sets given in this table should serve to illustrate the wide differences which could exist between apparently relatively good sets of force constants e.g. 4 and 5. It should also be noted that certain similarities appear to exist quite consistently throughout these sets. The most significant differences occur in the non-diagonal elements and in particular those involved in (C-C) stretching and (C-H) bending motion. Table (Q-X) contains the two types of parameters, i.e. those which the refinement process does not alter very significantly, set A; and those which are altered differently for different initial sets, set B.

Parabenzoquinone-d_4

A number of intermediate force fields as well as the final one were used in calculating the vibrational frequencies of parabenzoquinone-d_4, the results obtained from the latter are listed in table (Q-XI).

An attempt was also made to refine the quinone parameters using the deuterated compounds observed frequencies, the parameters obtained from this calculation are given in table (Q-XII).

Chloroquinone Planar Vibrations:

The potential energy parameters used in calculating the vibrational frequencies of the chloroquinones were initially transferred from set (II-A) given in table (Q-VIII-A). The diagonal stretching and bending constants were assumed to be 3.9×10^5 dyne cm^{-1} and 1.2×10^{-11} erg. respectively.

The non-diagonal terms involving (C-Cl) motion were all assumed to be equal to the corresponding (C-C) terms of parabenzoquinone, set (II-A).

The calculated frequencies of the chloroquinones; Table (Q-XIV) have a number of features in common.

1. One of the (C-Cl) stretches in the dichloroquinones and two in chloranil have values below 1000 cm^{-1}, around 850 cm^{-1}.
2. The (C-H) bending character is very much delocalised over all normal modes beyond 1000 cm^{-1} and to lesser extent the modes below 1000 cm^{-1}.

Refinement of Chloroquinone Force Field:

The refinement of the chloroquinones potential energy parameters, was carried out for individual compounds using the preferred assignments given in table (Q- VII).

In a number of cases convergence leads to similar values for certain parameters, common to two or more chloroquinones, but this is by no means always the case. When attempting to determine a preliminary force field for the chloroquinones, therefore, one is compelled to reject certain values of the refined parameters which disagree very significantly with the ones found for the other chloroquinones, and in parabenzoquinone itself. This of course assumes complete transferability of the force constants in the chloroquinone series. The bonding in the various quinones is nevertheless expected to change to a certain extent with different substitution patterns and it is not always a simple matter to say how such changes influence the various non-diagonal constants. It is possible nevertheless, to select a number of parameters which are found to remain unchanged or change only a little from one compound to another, it is thought that this set of parameters should in fact constitute the nucleus of a more general force field for these quinones. Table (Q- XIII).

Force Constants Used in calculating planar vibration frequencies for Parabenzoquinone

Table Q-VIII-A

	Serial number	I-A	II-A	I-B	II-B
α'	1	2.0121	2.0121	2.1302	2.1363
α''	2	2.0121	2.0121	1.8305	1.9800
$\alpha\alpha^{o}$	3	0.3610	0.3610	0.4528	0.4528
$\alpha\beta_{H}$	4	-	-	0.0000	0.0000
$\alpha\beta_{H}^{o}$	5	0.1897	0.1897	0.1960	0.1693
$\alpha\beta_{H}^{m}$	6	-	-	-0.0231	-0.0231
$\alpha\beta_{o}$	7	-	-	0.0000	0.0000
$\alpha\beta_{o}^{o}$	8	0.1897	0.1897	0.0184	0.0000
$\alpha\beta_{o}^{m}$	9	-	-	0.0000	0.0000
$\alpha\nu_{co}$	10	-0.3166	-0.3166	-0.2163	-0.3017
$\alpha\nu_{co}^{o}$	11	-	-	0.0000	0.0000
$\alpha\nu_{cc}^{o'}$	12	-0.2515	-0.2515	+0.3075	0.3075
$\alpha\nu_{cc}^{o''}$	13	-0.2515	-0.2515	0.2638	0.2638
$\alpha\nu_{cc}^{m'}$	14	-	-	0.0000	0.0000
$\alpha\nu_{cc}^{p}$	15	-	-	0.0000	0.0000
β_{o}	16	2.2830	1.9459	1.4003	1.7000
$\beta_{o}\beta_{o}^{p}$	17	-0.0173	-0.0173	-0.1276	-0.1000
$\beta_{o}\beta_{H}^{o}$	18	-0.0153	-0.0153	0.0000	0.0000
$\beta_{o}\beta_{H}^{m}$	19	0.0192	0.0192	-0.0088	0.0000
$\beta_{o}\nu_{cc}^{o}$	20	-0.0545	-0.0545	0.0000	0.0000
$\beta_{o}\nu_{cc}^{m}$	21	0.0534	0.0534	0.0000	0.0000
β_{H}	22	1.0170	1.0171	0.9999	1.0022
$\beta_{H}\beta_{H}^{o}$	23	0.0192	0.0192	-0.2539	-0.2567
$\beta_{H}\beta_{H}^{m}$	24	-0.0153	-0.0153	-0.1564	-0.1688
$\beta_{H}\beta_{H}^{p}$	25	-0.0173	-0.0173	0.1229	0.1229
$\beta_{H}\nu_{co}^{o}$	26	-0.2193	-0.2193	-0.1868	-0.1868
$\beta_{H}\nu_{co}^{m}$	27	0.0697	0.0697	-0.0199	-0.0199
$\beta_{H}\nu_{co}^{o''}$	28	-0.0545	-0.0545	0.3592	0.3592

Table (Q-VIIIA)(cont.)

$\beta \nu_{cc}^{o'}$	29	-0.0545	-0.0545	-0.1770	-0.1770
$\beta \nu_{cc}^{m}$	30	0.0534	0.0534	0.0231	0.0233
ν_{cc}'	31	3.4692	5.0348	5.4226	5.4226
ν_{cc}''	32	8.3392	7.9161	7.3000	7.3000
$\nu_{cc}\nu_{cc}^{o''}$	33	0.6333	0.6222	0.9854	0.9854
$\nu_{cc}\nu_{cc}^{o'}$	34	0.6333	0.2445	0.3003	0.3000
$\nu_{cc}\nu_{cc}^{m'}$	35	0.1133	-0.3021	-0.9561	-0.9570
$\nu_{cc}\nu_{cc}^{m''}$	36	0.1133	-0.0688	0.3000	-0.2000
$\nu_{cc}\nu_{cc}^{p'}$	37	0.5733	-0.0394	0.5004	0.5426
$\nu_{cc}\nu_{cc}^{p''}$	38	0.5733	0.0280	0.6840	0.5100
$\nu_{cc}\nu_{co}^{o}$	39	0.6333	0.7985	0.5900	0.5900
$\nu_{cc}\nu_{co}^{m}$	40	0.1133	-0.2052	-0.5186	-0.1786
$\nu_{cc}\nu_{co}^{p}$	41	0.5733	0.5733	0.1046	0.1046
ν_{co}	42	9.8187	10.0225	10.3001	10.4812
$\nu_{co}\nu_{co}^{p}$	43	0.0000	0.0000	0.0000	0.0000
ν_{CH}	44	5.0930	5.0930	5.0846	5.0846
$\nu_{CH}\nu_{CH}^{o}$	45	0.0250	0.0250	0.0250	+0.0250
$\nu_{CH}\nu_{CH}^{m}$	46	-0.0400	-0.0400	-0.0400	-0.0400
$\nu_{CH}\nu_{CH}^{p}$	47	0.0080	0.0080	0.01209	0.01209

Table (Q-VIIIB) (Cont)

The observed and calculated planar fundamentals of parabenzoquinone h_4 (Anno)

	Set I				Set II				
	Trial		Improved		Trial		Improved		Observed
a_g									
1	3066	4	3066	4	3063	1	3064	2	3062
2	1798	112	1719	33	1658	28	1665	21	1686
3	1691	24	1579	88	1616	51	1621	46	1667
4	1157	10	1144	3	1148	1	1147	0	1147
5	866	116	(770)	0	684	86	(770)	0	770
6	467	24	463	20	458	15	458	15	443
b_{1g}									
7	3044	0	3043	1	3044	0	3045	1	3044
8	1563	189	1422	48	1478	104	1582	208	1374
9	1288	77	1301	90	1307	44	1306	95	1211
10	666	66	685	85	689	89	684	84	600
11	377	99	385	9	501	25	497	21	476
b_{2u}									
12	3071	9	3070	8	3071	9	3072	10	3062
13	1836	168	(1668)	0	1662	6	(1668)	0	1668
14	1434	80	1901	47	1426	72	1446	92	1354
15	1028	84	979	35	1006	62	1040	96	944
16	767	39	713	15	761	33	777	49	728
b_{3u}									
17	3082	20	3082	20	3083	21	3082	21	3062
18	1580	12	(1592)	0	1601	9	(1592)	0	1592
19	1270	29	1171	128	1216	83	1343	44	1299
20	1135	69	1067	1	1149	83	1155	89	1066
21	311	97	(408)	0	423	15	(408)	0	408
$\sum\lvert(\nu^{\circ}-\nu)\rvert/N-3$		58.9		30.2		42.2		42.5	

Table (Q-VIIIC) (Cont.)

The Observed and Calculated Planar Fundamentals of parabenzoquinone d_4 (Anno)

		Set I				Set II			
	Observed	Trial		Improved		Trial		Improved	
a_g									
1	2290	2299	9	2298	8	2289	2	2289	2
2	1668	1783	115	1675	7	1616	52	1629	39
3	1657	1650	7	1594	103	1595	62	1598	59
4	828	906	78	857	29	846	18	858	30
5	746	790	44	725	21	645	92	723	23
6	433	461	28	457	24	452	19	453	20
			281		192		245		172
b_{1g}									
7	2277	2275	2	2269	8	2272	5	2277	0
8	1318	1515	197	1370	52	1431	113	1537	219
9	919	997	78	1033	114	1033	114	1023	104
10	582	646	64	659	77	663	81	662	80
11	464	357	107	456	8	471	7	466	2
			448		259		320		421
b_{2u}									
12	2277	2287	10	2283	6	2285	8	2287	10
13	1662	1835	173	1667	5	1660	2	1666	4
14	1160	1255	95	1182	22	1235	75	1281	121
15	873	875	2	868	5	869	4	872	91
16	635	705	70	654	19	679	44	717	82
			350		57		133		218
b_{3u}									
17	2277	2300	23	2301	24	2305	28	2305	28
18	1560	1532	28	1531	29	1539	21	1536	24
19	1253	1230	28	1079	179	1201	57	1326	88
20	793	833	40	832	39	835	42	635	42
21	402	309	93	403	1	419	17	404	2
$\sum\|(\nu^\circ-\nu)\|/N-3$		61.5	212	37.1	272	41.2	165	47.5	184

Sets of Force Field Parameters for Parabenzoquinone

Table (Q-IX-A)

	1	2	3	4	5
1	2.1303			2.0121	2.0639
2	1.8632			2.0121	1.8727
3	0.4372			0.3610	0.3610
4	0.0500			0.0000	0.0000
5	-0.1961			-0.2927	-0.2747
6	-0.0231			0.0000	0.0000
7	0.0000			0.0000	0.0000
8	-0.0445			0.1890	0.1897
9	0.0701			0.0000	0.0006
10	-0.2661			-0.3160	-0.9000
11	0.0000				-0.0715
12	0.2854			-0.2515	0.0225
13	0.2129			-0.2515	-0.2599
14	0.0000				0.1688
15	0.0000				-0.0391
16	1.7803			1.9459	1.7633
17	-0.1276			-0.0173	-0.1362
18	0.0000			-0.0153	-0.0196
19	-0.0887			0.0782	0.1232
20	0.0000			- 0.6189	-0.6188
21	0.0000			-0.2346	-0.1615
22	1.0000			1.0171	1.0126
23	-0.1656			-0.0811	-0.0811
24	-0.1289			-0.0545	0.0151
25	0.1430			-0.0173	-0.0173
26	-0.2630			-0.7387	-0.7386
27	0.0369			0.1071	0.1071
28	-0.0084			0.1561	0.1561
29	0.1351			-0.1420	-0.1420
30	-0.0387			0.0534	0.0344
31	5.4647		5.0303	5.0348	5.0348
32	7.2428		6.7698	7.9161	7.8359
33	0.7999			0.5510	0.5661
34	0.6003			0.7804	0.7462
35	0.4183			0.1477	0.2073
36	-0.5409			-0.4761	-0.4343
37	0.3005	-0.0697		0.0414	0.0413
38	0.2840	-0.7637		-0.3777	-0.3777
39	0.5240			0.7088	0.7088
40	-0.1780			-0.1633	-0.1633
41	0.1046			0.1350	0.1349
42	10.3001			10.0225	10.0225
43	0.0000			0.0000	0.0000
44	5.0702			5.0930	5.0930
45	0.0175			0.0250	0.0117
46	0.0175			-0.0400	0.0119
47	-0.0184			0.0080	0.0080

Table (Q-IX-B) Cont.

Calculated Planar Vibrations of Parabenzoquinone

Obs.	1	2	3	4	5
3062	3061	3061	3061	3044	3063
1668	1662	1662	1661	1710	1673
1354	1244	1257	1241	1337	1339
944	941	950	938	1021	930
728	715	720	714	744	727
3044	3041	3041	3040	3071	3058
1373	1463	1422	1373	1377	1379
1211	1191	1191	1190	1221	1198
600	642	638	631	628	624
476	478	475	472	518	471
3062	3063	3062	3061	3062	3076
1686	1741	1685	1668	1692	1687
1667	1676	1665	1645	1673	1652
1147	1292	1255	1243	1177	1193
770	376	853	830	779	696
443	470	466	464	452	450
3062	3064	3066	3065	3082	3063
1592	1517	1573	1545	1588	1593
1299	1314	1390	1325	1287	1303
1066	1060	1076	1070	1065	1075
408	392	395	392	437	430

Table (Q - X)

A list of the Two Major Types of Force
Constants used in the Quinone
Calculations.

-A-

1	α'
2	α''
3	$\alpha\alpha^{o}$
4	$\alpha\beta_{H}$
5	$\alpha\beta_{H}^{o}$
6	$\alpha\beta_{H}^{m}$
7	$\alpha\beta_{O}$
9	$\alpha\beta_{O}^{m}$
10	$\alpha\nu_{CO}$
14	$\alpha\nu_{CC}^{m''}$
15	$\alpha\nu$
16	β_{O}
18	$\beta_{O}\beta_{H}^{o}$
19	$\beta_{O}\beta_{H}^{m}$
22	β
31	ν_{CC}'
32	ν_{CC}''
33	$\nu_{CC}\nu_{CC}^{o''}$
34	$\nu_{CC}\nu_{CC}^{o'}$
36	$\nu_{CC}\nu_{CC}^{m''}$
39	$\nu_{CC}\nu_{CO}^{o}$
40	$\nu_{CC}\nu_{CO}^{m}$
41	$\nu_{CC}\nu_{CO}^{p}$
42	ν_{CO}
43	$\nu_{CO}\nu_{CO}$
44	ν_{CH}
45	$\nu_{CH}\nu_{CH}^{o}$
46	$\nu_{CH}\nu_{CH}^{m}$
47	$\nu_{CH}\nu_{CH}^{p}$

Sets I-B, II-B and III-B in part (B) of this table were obtained from set I-A by a least squares calculation.

Table (Q- X)(Cont.)

- B -

No.	Description	I-A	II-A	I-B	II-B	III-B
8	$\alpha\beta_o^o$	0.1897	0.1897	-0.0184	-0.0000	0.0172
12	$\alpha\nu_{cc}^{o'}$	-0.2515	-0.2515	0.3075	0.3075	0.3075
13	$\alpha\nu_{cc}^{o''}$	-0.2515	-0.2515	0.2638	0.2638	0.2638
17	$\beta_o\beta_o^p$	-0.0173	-0.0173	-0.1276	-0.1000	0.0000
20	$\beta_o\nu_{cc}^o$	-0.0545	0.0000	0.0000	0.0000	-0.0255
21	$\beta\nu_{cc}^m$	0.0534	0.0534	0.0000	0.0000	0.0000
23	$\beta_H\beta_H^o$	0.0192	0.0192	-0.2539	-0.2567	-0.2670
24	$\beta_H\beta_H^m$	-0.0153	-0.0153	-0.1564	-0.1688	-0.1688
25	$\beta_H\beta_H^p$	-0.0173	-0.0173	0.1229	0.1229	0.1229
26	$\beta_H\nu_{co}^o$	-0.2193	-0.2193	-0.1868	-0.1868	-0.1868
27	$\beta_H\nu_{co}^m$	0.0697	0.0697	-0.0199	-0.0199	0.0199
28	$\beta_H\nu_{cc}^{o''}$	-0.0545	-0.0545	0.3592	0.3592	0.3592
29	$\beta\nu_{cc}^{o'}$	-0.0545	-0.0545	-0.1770	-0.1770	-0.1770
30	$\beta\nu_{cc}^m$	0.0534	0.0534	0.0231	0.0233	0.0233
35	$\nu_{cc}\nu_{cc}^{m'}$	0.1133	-0.3021	-0.9561	-0.9570	-0.9561
37	$\nu_{cc}\nu_{cc}^{p'}$	0.5733	-0.0394	0.5004	0.5426	0.5426
38	$\nu_{cc}\nu_{cc}^{p''}$	0.5733	0.0280	0.6040	0.5100	0.5100
			$\sum\nu/_{N-3}$:	12.2	20.7	17.0

Calculated Planar Frequencies of Parabenzoquinone-d_4

Table (Q- XI)

	Obs.	Calc.
1	2290	2289
2	2277	2289
3	2277	2286
4	2277	2254
5	1668	1686
6	1662	1653
7	1657	1610
8	1560	1455
9	1318	1341
10	1253	1185
11	1160	1174
12	919	1064
13	873	840
14	828	831
15	793	769
16	746	759
17	635	645
18	582	618
19	464	472
20	433	419
21	492	335

Force Constants used in Calculating Planar Frequencies of Parabenzoquinone-d_4

Table (Q- XII)

1	2.4119	25	0.1229
2	1.8305	26	-0.1860
3	0.4528	27	-0.0199
4	0.0000	28	0.3592
5	-0.1960	29	-0.1770
6	-0.0231	30	0.0233
7	0.0000	31	5.4226
8	0.0184	32	7.3000
9	0.0000	33	0.9854
10	-0.2163	34	0.3003
11	0.0000	35	-0.9556
12	0.3075	36	0.3000
13	0.2638	37	0.5005
14	0.0000	38	0.6840
15	0.0000	39	0.5901
16	1.4003	40	-0.1787
17	-0.1276	41	0.1046
18	0.0000	42	10.3001
19	-0.0887	43	0.0000
20	0.0000	44	5.0846
21	0.0000	45	0.0363
22	0.9999	46	-0.0400
23	-0.2539	47	0.0121
24	-0.1564		

Force Constants Used in calculating the Planar Frequencies of some Chloroquinones.

Table (Q- XIII)

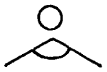
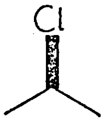
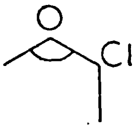
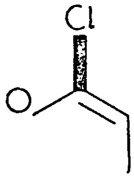
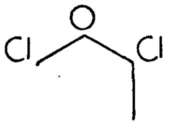
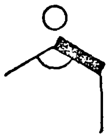
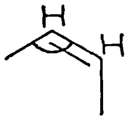
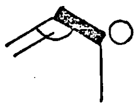
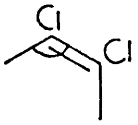
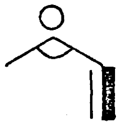
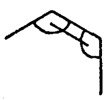
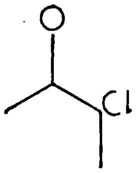
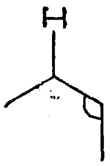
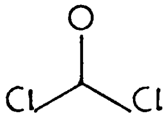
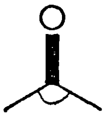
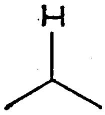
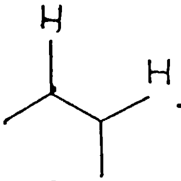
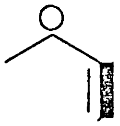
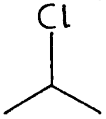
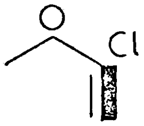
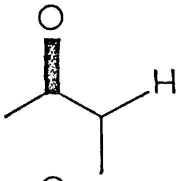
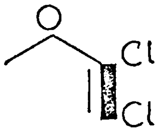
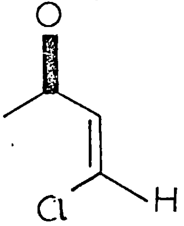
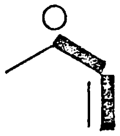
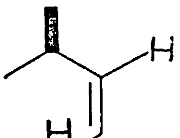
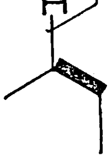
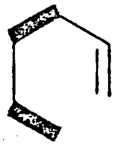
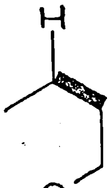
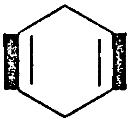
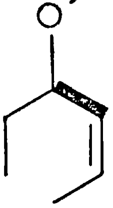
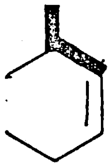
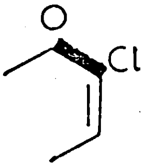
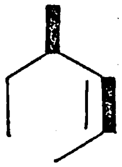
1		1.9800	9		-0.2935
2		2.0660	10		0.2831
3		2.4275	11		0.3000
4		2.0848	12		-0.4927
5		2.1446	13		-0.1389
6		0.3508	14		1.9250
7		-0.1986	15		2.2663
8		-0.3166	16		1.0171

Table (Q- XIII)(Cont.)

17		-0.2670	26		7.2000
18		1.1372	27		7.0072
19		-0.0368	28		7.3212
20		0.2753	29		0.8554
21		-0.1241	30		-0.2677
22		0.1896	31		-0.2000
23		-0.0160	32		0.8000
24		4.1679	33		0.6140
25		5.2283	34		-0.1787

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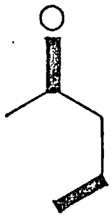
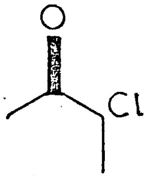
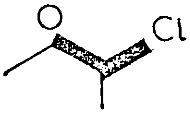
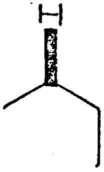
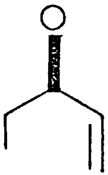
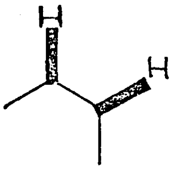
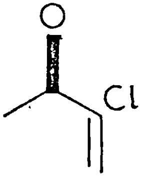
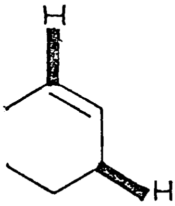
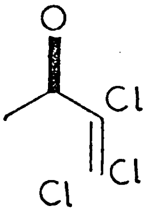
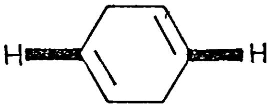
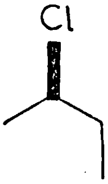
35		0.2019	41		5.1222
36		0.4362	42		5.0930
37		9.5670	43		0.0250
38		9.7730	44		-0.0117
39		9.7910	45		0.0070
40		3.9000			

A bold line denotes a stretch and a thin one a bend ofthe type β(C-X).

Table (Q-XIV)Cont.

Calculated Planar Vibrations of some Chloroparabenzoquinones

	Calc.	Calc.	Calc.	Calc.
	2Q	23Q	25Q	26Q
1	3078 1*	3072 1*	3077 1*	3076 1*
2	3060 1	3058 1	3070 1	3070 1
3	3050 1	1680 2	1710 2 3	1710 2 4 6
4	1696 2 3 5	1636 2 3 4	1664 2 3 6	1655 2 3
5	1673 4 3 2	1624 2 3 4	1605 3	1611 4 3
6	1597 2 4 5	1571 3	1564 4	1570 4
7	1552 2 4 6	1362 5 3 4	1363 3 5	1317 4 5 8
8	1446 4 5	1282 3 5	1318 4 5	1291 5
9	1341 5 4	1272 5 7	1225 5	1272 5 7 8
10	1211 5 4 6	1237 5 6 3	1187 5 3 7	1136 3 5
11	1162 5 7 4	1116 5 7 4	1080 7 4 6	1090 3 6 7
12	1119 5 4	1033 7	1033 5 7	945 7
13	1064 4 5 7 8	954 6 7 5	922 6 7	902 7 6
14	879 7 5 8	754 6	726 6	800 6
15	788 6 7 5	592 6 8 9	571 6 7 8 9	610 6 8 9
16	744 6 5	524 6 7	509 7 8 6	520 8 6
17	557 6 8	445 8 6	481 8 6	481 6 8 7
18	502 8 6	356 8 6 7	339 8	360 6
19	442 8 6	326 8 6	297 9 8	339 8
20	331 8	230 9	222 9 8	206 9 8
21	229 9	148 9	177 9	158 9

*These figures indicate contributions from the internal co-ordinates labelled 1: ν(C-H), 2: ν(C-O), 3: ν(C=C), 4: ν(C-C), 5: β(C-H), 6: α(C-C-C), 7: ν(C-Cl), 8: β(C-O), 9: β(C-Cl), Scherers report on the force field for out-of-plane vibrations of a number of chlorobenzenes is not accompanied by CDF or PED. Examination of the PED given table (Q - XV) which is obtained from their potential energy parameters - which produces almost exactly their calculated frequencies - shows that the lowest fundamental which appears to have been quite unambiguously assigned as an out-of-plane (C-Cl) bend, contains an extremely large amount of (C-C) torsional motion. The same is true for frequency ν_8; on the other hand, the modes labelled ν_5 and ν_6 seem to receive a good deal of γ(C-Cl) participation.

The same pattern is observed on transferring the above force field parameters to the p-difluorobenzene problem, with the refined parameters, and again when the refined force field for p-difluorobenzene is used for the p-benzoquinone calculation.

The amount of (C-C) torsion and (C-Cl) out-of-plane contributions in the lowest two modes and modes ν_5 and ν_6, respectively are not of sufficient magnitude to make one doubt the validity of the force constants developed for the chlorobenzenes, which are based on a comprehensive study of a considerable number of chlorobenzenes and deuterated chlorobenzenes, but it should be recognised, nevertheless, that the (C-C) and (C-Cl) out-of-plane vibrations do mix in this way when this force field is used.

Out-of-plane Vibrations of Parabenzoquinone:

The force field developed by Scherer[25] which is based on a study of a large number of chlorobenzenes was used as a zero order approximation for calculating refined force fields for p-dichloro and p-difluorobenzene which were in turn used for p-benzoquinone - calculated sets IIA and IIB, table (Q- XVIB). The internal co-ordinates used by Scherer are identical to those defined by Wilson Decius and Cross[17] and used in this work so that no transformation of the force constants was necessary. The Scherer Valence Force Field (SVFF) was preferred to that put forward by Radcliffe and Steele[43] for p-dihalobenzenes because the former is based on a very much larger number of compounds and produces better agreement with the observed frequencies of the chlorobenzenes. Both force fields are in general agreement with one another and with the force fields of Miller and Crawford[41] and that of Kakuti and Schimanouchi[42].

The experimental value of the frequencies of the out-of-plane fundamentals of p-difluoro and p-dichlorobenzene used in this work are those reported by Lippincott[40].

The force field for parabenzoquinone was further "improved" by introducing additional parameters to the original Scherer force field to take into account interactions between co-ordinates in the para-position with respect to one another,- Table (Q- XVII).

The assignments put forward by Prichard[27] and Anno[20] for the non-planar vibrations of parabenzoquinone are given in table (Q- XVIII). Those suggested by Anno are supported by data from the vapour and solution spectra of a number of deuterated derivatives, and are therefore used in the determination of an improved set of force constants for use in the calculation of the fundamentals of the other quinones and diazo-oxides. The experimental frequencies of the non-planar fundamentals of parabenzoquinone-d_4,[27, 20] are given in table (Q-XIX) together with the values of the frequencies calculated by Anno from Sadô's force field[20]. No force field refinement has so far been reported by Anno, the average difference $\sum(\nu^i - \nu^o)/N$ is 28.6 cm^{-1} for parabenzoquinone-h_4 and 35.4 cm^{-1} for parabenzoquinone-d_4, and no PED or CDF were produced in the above mentioned report.

In order to investigate the degree of dependence of the force field parameters upon the assumed sets of experimental frequencies the refinement process was carried out using three different sets of observed frequencies, these sets together with the calculated frequencies are listed in table (Q-XXI) and the appropriate force field parameters are given in table (Q-XXII). The first set of experimental frequencies used is almost identical to the one suggested by Prichard and the second is obtained from the first replacing the highest mode with the value suggested by Anno for this assignment, the third set of frequencies is derived from Anno's assignments.

All three sets of force constants appear to produce potential energy distribution figures which indicate a considerable amount of (C-C) torsion characters in the low lying modes, the third force field is preferred to the other two since it does not contain the rather anomalously low (C-C) diagonal constant typical of the other two. It should also be noted that the third set of parameters seems to be in better agreement with the dichlorobenzene and difluorobenzene force fields given in table (Q-XVII).

Table (Q-XX) contains a set of frequencies calculated for parabenzoquinone using a set of force constants based on the SVFF developed in this work for paradifluorobenzene, set (IV) table (Q - XVII).

Parabenzoquinone-d_4

Sets I, II, III and IV of table (Q - XVII) were used in calculating the vibrational frequencies of parabenzoquinone-d_4, it was found that the magnitude of the discrepancy between the calculated and experimental values of the frequencies suggested by Anno, is somewhat large, for all these sets. Table (Q- XX) contains the frequencies calculated from set IV of table (Q- XVII).

The Chloroquinones:

The calculated non-planar vibrations of the chloroquinones are given below - table (Q- XXIII) - together with the corresponding results for the similarly substituted chlorobenzenes.

Table (Q- XXIV) contains the calculated and observed frequencies of four of the chloroquinones considered in this work. The force constants used in these calculations are a mixture of the ones put forward by Scherer[25] for a large number of chlorobenzenes, and, where (C-O) vibrations are involved, the (C-F) force constants found for paradifluorobenzene - table (Q- XVII) - were used.

Table (Q- XV)

Potential Energy Distribution for p-Dichlorobenzene

	1	2	3	4	5	6	7	8	9
	a_u	b_{3g}	b_{1u}	b_{2g}	b_{3g}	b_{1u}	a_u	b_{3g}	b_{1u}
	951	934	819	815	687	485	407	298	115
101	0.03	0.15	0.00	0.15	0.97	0.79	0.44	0.03	0.46
202	0.06	0.07	0.00	0.00	0.48	0.00	0.84	0.09	0.00
102	0.02	0.09	0.00	0.03	0.86	0.20	0.34	0.02	0.12
707	0.00	0.05	0.00	0.19	0.63	1.18	0.00	0.80	0.21
808	1.22	1.30	1.13	1.20	0.16	0.06	0.30	0.08	0.21
708	0.00	0.12	0.00	0.25	0.19	-0.13	0.00	-0.12	-0.11
709	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.01
710	0.22	0.23	-0.19	-0.22	0.03	-0.01	0.05	0.01	-0.03
809	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
812	-0.04	0.04	-0.02	0.02	0.00	0.00	-0.01	0.00	0.00
811	-0.53	-0.72	0.00	-0.40	-1.04	0.18	-1.22	-0.10	-0.32
108	0.00	-0.10	0.00	-0.22	-1.18	-1.49	0.00	0.17	0.40
109	-0.06	-0.13	0.00	0.00	-0.12	0.00	0.00	-0.02	0.00
310	0.00	-0.03	0.00	0.00	-0.29	0.00	0.00	-0.06	0.00

* The force constants are denoted by numbers given by the expression (100nXm) where n and m refer to the internal co-ordinates, which are numbered in the manner shown in figure (NCA- I).

Non-planar Force Field Parameters for Paradifluoro – and Paradichlorobenzene

Table (Q-XVI A)

	Description	p-DICl[25]	DIF
1	101	0.269	0.2721
2	202	0.259	0.2484
3	102	-0.065	-0.0650
4	103	0.000	0.0001
5	104	0.000	0.0000
6	205	0.000	0.0000
7	707	0.579	0.5836
8	808	0.429	0.4233
9	708	-0.091	-0.0920
10	709	0.006	0.0027
11	710	-0.016	-0.0220
12	809	-0.072	-0.0720
13	812	0.003	0.0115
14	811	-0.014	-0.0140
15	108	-0.152	-0.1522
16	209	-0.152	-0.1522
17	310	-0.148	-0.1847
18	109	0.035	0.0335
19	608	0.035	0.0335
20	210	0.053	0.0541
21	211	0.000	0.0000
22	110	0.000	-0.0002

Calculated Frequencies of Non-planar Vibrations of Paradichloro and Paradifluorobenzene

Table (Q- XVI B)

(A) Paradichlorobenzene

Obs.	Calc. (I)	Calc. (II)
951	947	952
934	928	934
819	818	820
815	813	815
687	691	687
485	483	484
407	406	406
298	305	303
115	108	107

(B) Paradifluorobenzene

Obs.	Calc. (I)	Calc. (II)	Calc. (III)	Calc. (IV)
943	930	939	951	942
928	919	928	934	932
833	834	834	826	835
800	792	803	820	804
699	699	703	693	699
509	494	509	510	508
405	354	375	405	404
375	342	349	359	363
170	166	168	155	155

Force Field Parameters for Non-planar Vibrations of P-$X_2C_6H_4$ species

Table (Q-XVII) Cont.

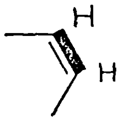
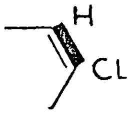
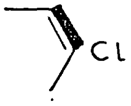
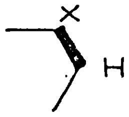
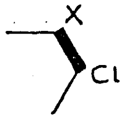
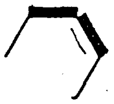
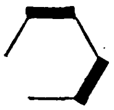
			SVFF I	SVFF II	DIF III	DIF IV*
1			0.259	0.2622	0.2721	0.2756
2			0.269			
3			0.347			
4	‡					
5	‡					
6			-0.065	-0.0647	-0.0650	-0.0394
7	‡					
8	‡		0.000	0.0000	-0.0001	-0.0030

Table (Q-XVII)(Cont.)

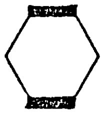
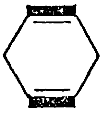
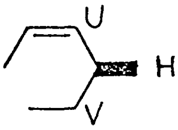
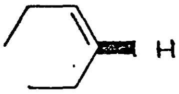
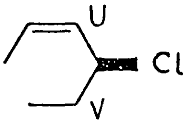
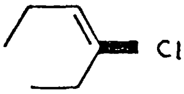
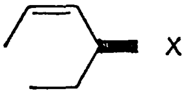
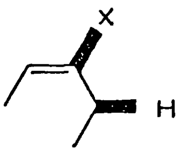
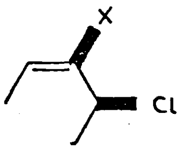
			SVFF-I	SVFF-II	DIF-III	DIF-IV
9		+ +	0.000	0.0000		
10		+ +	0.000	0.0000		
11			0.448 + 0.429 ⬠ 0.414 ⊖	0.4295	0.4233	0.4470
12						
13			0.579 + 0.541 ⬠ 0.506 ⊖	0.5725	0.5836	0.4540
14						
15						
16						
17						

Table (Q-XVII)(Cont.)

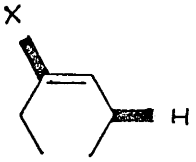
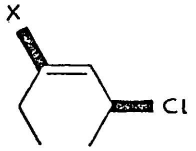
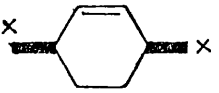
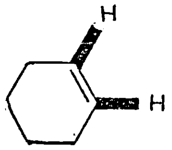
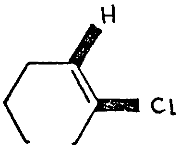
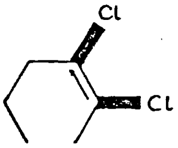
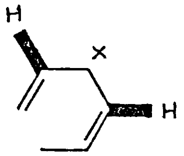
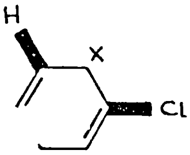
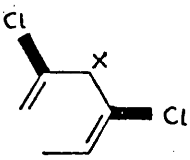
		SVFF-I	SVFF-II	DIF-III	DIF-IV
18					
19					
20					
21		-0.072	-0.0718	-0.0720	-0.0003
22		-0.092	-0.0926	-0.0920	
23		-0.066			
24		0.003 ●	0.0030	0.0115	0.0640
25		0.003 ●	0.0030	0.0115	0.0640
26					

Table (Q-XVII)(Cont.)

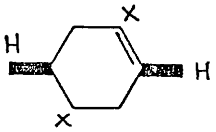
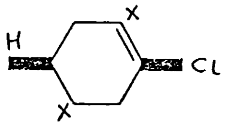
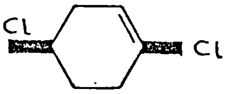
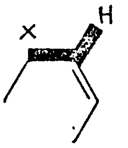
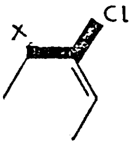
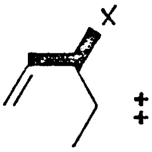
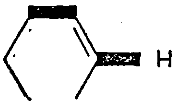
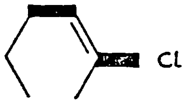
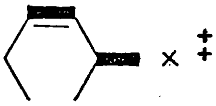
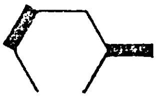
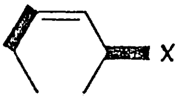
		SVFF-I	SVFF-II	DIF-III	DIF-IV
27		-0.014●	-0.014	-0.0140	-0.0140
28		-0.021 ●			
29		-0.016	-0.0174	-0.0220	-0.0070
30		-0.152●	-0.1521	-0.1517	-0.1500
31		-0.184●	-0.1841	-0.1847	-0.1500
32					
33		0.035	0.0350	0.0335	0.0040
34		0.053	0.0526	0.0541	0.0004
35					

Table (Q-XVII)(Cont.)

		SVFF-I	SVFF-II	DIF-III	DIF-IV
36	 ‡		0.0000	0.0000	0.0110
37	 ‡		0.0000	-0.0002	0.0110

* SVFF: Scherer's Valence Force Field

DIF: Difluorobenzene Force Field

‡ Parameter does not originate from Scherer's force field.

+ U : H ; V : H

○ U : H ; V : Cl

⊖ U : Cl ; V : Cl

◐ The letter x refers to a hydrogen atom in the case of the benzene derivatives and to an oxygen atom in the case of the quinones.

Table (Q-XVIII)

Non-planar Fundamentals of Parabenzoquinone and Parabenzoquinone-d_4.

Symmetry	Anno	Prichard	Anno	Prichard
b_{2g}	998	1004	843	
a_u		932		
b_{1u}	882	884	793	796
b_{2g}	794	794	711	
b_{2g}	745	610	574	
b_{1u}	505	508	418	
a_u		402		
b_{2g}	241	243	228	
b_{1u}	108	108	106	

Table Q-XIX

Calculated and Observed Frequencies of Parabenzoquinone and Parabenzoquinone-d_4

	PBQ-h_4		PBQ-d_4	
	Obs.	Calc.	Obs.	Calc.
a_u	-	958	-	738
	-	397	-	363
b_{1u}	882	862	793	737
	505	539	418	464
	108	98	106	96
b_{2g}	794	831	574	645
b_{3g}	998	955	843	826
	745	789	711	679
	291	244	228	234
$\sum\lvert(\nu^\circ-\nu)\rvert/N-3$		28.6		35.4

Calculated Non-planar Fundamental Frequencies of Parabenzoquinone-h_4 and Parabenzoquinone-d_4

Table (Q- XX)

		PBQ-h_4		PBQ-d_4	
	Symmetry	Obs.	Calc.	Obs.	Calc.
1	b_{3g}	998	955	843	826
2	a_u		958		738
3	b_{1u}	882	862	793	737
4	b_{3g}	794	789	711	672
5	b_{2g}	745	831	574	464
6	b_{1u}	505	539	418	464
7	a_u		397		363
8	b_{3g}	241	244	228	234
9	b_{1u}	108	98	106	96

Non-planar Fundamentals of Parabenzoquinone-h_4 Calculated Using Various Sets of Force Constants

Table (Q- XXI)

	Set I	Calc.	Set II	Calc.	Set III	Calc.
1	958	958	998	997	998	993
2	932	933		957	969	953
3	884	886	884	884	882	891
4	794	801	794	799	794	802
5	610	610	610	619	745	741
6	508	507	508	515	508	510
7	402	389	402	387	402	408
8	243	243	243	250	241	248
9	108	160	108	161	108	164

Table Q-XXII

Non-planar Quinone Force Field parameters

Serial Number	Set I	Set II	Set III	Set IV
1	0.2352	0.2264	0.2342	0.2350
2	0.1624	0.1647	0.2352	0.3136
3	-0.0481	-0.0478	-0.0628	
4	0.0000	0.0000	0.0000	
5	0.0000	0.0000	0.0000	
6	-0.0488	-0.0461	-0.1455	-0.0609
7	0.6305	0.6331	0.6262	
8	0.4377	0.4523	0.4433	
9	-0.1102	-0.1102	-0.1069	
10	0.0039	0.0174	0.0039	
11	-0.0192	-0.0275	-0.0253	
12	-0.0700	-0.0787	-0.0700	
13	0.0166	0.0214	0.0144	
14	-0.0048	-0.0011	0.0019	
15	-0.1537	-0.1568	-0.1545	
16	-0.1537	-0.1568	-0.1545	
17	-0.1707	-0.1707	-0.1724	
18	0.0271	0.0271	0.0285	
19	0.0271	0.0244	0.0244	
20	0.0541	0.0541	0.0537	
21	0.0000	0.0000	0.0000	
22	0.0000	0.0000	0.0000	

Calculated
Non-planar Vibrational Frequencies of some Chloroquinones and some similar Chlorobenzenes.

Table (Q-XXIII)

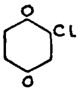
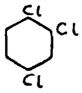
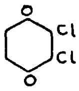
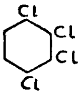
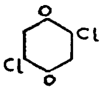
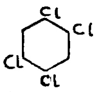
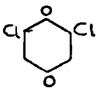
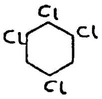
No.								
1	948	942	926	940	910	878	909	871
2	904	869	846	808	896	878	901	859
3	836	811	605	706	697	681	679	694
4	632	688	588	557	576	600	621	560
5	551	551	405	530	445	442	409	520
6	395	435	320	307	396	348	377	316
7	300	305	214	240	184	225	232	215
8	172	183	150	116	177	140	171	147
9	136	117	83	89	106	80	86	80

Table (Q-XXIV)

Observed and Calculated Frequencies of some Chloroquinones

	2Q		23Q		25Q		26Q	
No.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	996	948	994	926	948	910	905	909
2	913	904	848	849	899	896	882	901
3	834	836	582	605	602	697	667	679
4	641	632	532	588	597	576	487	621
5	604	551	468,354	405	346	445	304	409
6	372	395	263	320	240	396	259	377
7	271	300	120	214	162	184	124	232
8	180	172	134	150	197	177	197	171
9	80	136	82	83	103	106	106	86

Refinement of the Non-planar quinone force constants.

Two different sets of force constants were used in this work, table (Q-XXV). Apart from allowing distinction between parameters 17, 18 and 20 and 21, the first set has exactly the same form that Scherer uses for p-dichlorobenzene[25]. The second set, however takes into account four additional types of interaction parameters. The experimental data used in the refinement are the assigned spectra of parabenzoquinone and four of its deuterated derivatives[20].

The least squares method outlined earlier was thus used in conjunction with the experimental frequencies of parabenzoquinone-h_4 only (A) and using all 45 experimental frequencies of parabenzoquinone-h_4 -d_4, (26)-d_2, (25)-d_2 and parabenzoquinone-d_1.

The final force constants from these refinement attempts are given in table (Q-XXVI). The parameters of sets A and B possess certain differences among themselves and they both differ in a number of points from the force field parameters found for the paradisubstituted benzenes by other workers and in this work, Table (Q-XVII). These differences are nevertheless seen to be consistent with the different bonding arrangements in these compounds. The disagreement between the two sets A and B are almost certainly due to the different number of constraints used in their calculation, and the parameters of set B should clearly be more reliable since they satisfy five times the number of experimental points which were used in calculating set A.

The results obtained from the refinement of the non-planar force field parameters of the quinones as given in set II table (Q-XXVII), differ in certain points from the parameters which have been found for paradisubstituted benzenes.

The most important differences are those involving the interaction terms related to the γ(C=O) bending and the torsion about the (C=C) bond as compared to the interaction terms of the γ(C-X) and the torsions about the (C-C) bond in the dihalobenzenes. The remaining elements of the quinone force field, however, appear to be in general agreement with the corresponding parameters of paradichlorobenzene, for example. The non-diagonal term corresponding to the interaction between the two (C=O) groups differs quite considerably from its counterpart in the dichlorobenzene force field since it has a small positive value in the former and an almost equal but negative value in the latter. This might be taken to mean that the out-of-plane bending of one of the (C=O) groups results in a greater resistance towards the bending of the opposite (C=O) group, while the reverse is true in the case of the para disubstituted benzenes. Other departures from the para substituted benzene force field might be thought of as contributing to a picture in which the out-of-plane bending of one of the (C=O) groups leads to a generally more rigid structure elsewhere in the molecule.

It is dangerous, however, to read too much physical significance into these interaction terms since they are not, as yet, very well understood.

The parameters given in table (Q-XXVI) set-I depart from the previous two sets (II-A and II-B) in a number of points. The γ(C=O) force constant for example has much higher value in set I than in the other two sets, and the interaction term f $[\gamma(C-H)/\gamma(C-H)]^{P}$ is negative which corresponds more closely with the value of this parameter found in the paradihalobenzene series. These features are thought to originate from the general similarity between the two types of force fields, a property which is not shared by sets (II-A) abd (II-B) which in addition to distinguishing between the two types of (C-C) bonds in all the cross terms, take into account a number of additional non-diagonal force constants. This point is of the utmost importance when it comes to comparing the parameters obtained from the force fields developed in this work with force fields developed with different interactions equated or not taken into account. The force field given as set I in table (Q-XXVI) agrees with the previous sets in that it has a positive nature for the constant f $[\gamma(C=O)/\gamma(C=O)]$. The persistance of this behaviour in all the force fields tried for parabenzoquinone and its transferability to the chloro substituted quinones might be taken to mean that a positive value for this force constant is possibly a property of the parabenzoquinone force field.

An experiment designed to investigate the importance of the various non-diagonal parameters in influencing the agreement between the calculated and observed frequencies, shows that both the γ(C=O)/γ(C=O) and $[\gamma(C=O)/\gamma(C-H)]^{m}$ terms are not very important. The non-planar frequencies of parabenzoquinone $-h_4$ and $-d_4$ calculated using set I of table (Q-XXVI) after parameters 7 and 8 have been set to zero, have an average difference from the observed frequencies of about 7 cm^{-1}. The meta- and para- $[\gamma(C-H)/\ \gamma(C-H)]$ interaction terms are, however, more important in influencing the agreement between the calculated and observed frequencies of the (C-H) deformations in particular, the former being more so than the latter.

An attempt was made to calculate a set of force field parameters that ignores all $[\gamma(C-X)/\ \gamma(C-H)]$ cross terms other than those involving substituents in the ortho position with respect to one another. The resulting force constants, set II, and frequencies are given in table (Q-XXVII). The agreement with the observed results is not as well as it is for the force fields mentioned above, and further improvement in the fit between the experimental and calculated frequencies takes place only very slowly.

A further attempt was made at calculating an even more abbreviated force field, by equating parameters 8 and 9 and 11 and 12 in set II, table (Q-XXVII). This in fact amounts to considering the interactions between the torsions about (C=C) and (C-C) and the (C-H) deformation equivalent. This model is found to be less adequate than the previous one and it is, therefore, concluded that the best valence force field for the non-planar vibrations of p-benzoquinone and its deutero derivatives is in fact the one given as set I in table (Q-XXVI).

Table (Q- XXV)

Zero-order Parameters used in the Refinement of the Non-planar Quinone Force Field

Number	Description	Set I	Set II
1	101	0.259	0.259
2	202	0.259	0.259
3	102	-0.065	-0.065
4	304		0.065
5	105		0.000
6	103		0.000
7	104		0.000
8	205		0.000
9	707	0.579	0.579
10	808	0.429	0.429
11	708	-0.091	0.091
12	709	0.006	0.006
13	710	-0.021	-0.021
14	809	-0.072	-0.072
15	812	0.003	0.003
16	811	-0.014	-0.014
17	108	-0.152	-0.152
18	209	-0.152	-0.152
19	310	-0.184	-0.184
20	109	0.035	0.035
21	608	0.035	0.035
22	210	0.053	0.053
23	211		0.000
24	312		0.000
25	110		0.000

Table (Q- XXVI)

Refined Force Constants Calculated for the Non-planar Vibrations of Parabenzoquinone

No.	Set I	No.	Set II	
			(A)	(B)
1	0.1344	1	0.1773	0.1653
2	0.2720	2	0.2793	0.2817
3	-0.0656	3	-0.0616	-0.0574
		4	-0.0484	-0.0476
		5	0.0017	0.0020
		6	0.0075	0.0049
		7	-0.0062	-0.0125
		8	-0.0945	-0.0914
4	0.6548	9	0.4722	0.4727
5	0.4507	10	-0.4356	-0.4467
6	-0.1419	11	-0.1468	-0.1439
7	0.0015	12	0.0153	-0.0001
8	0.0135	13	0.0435	0.0803
9	-0.1379	14	-0.1017	-0.1117
10	0.0123	15	0.0231	0.0228
11	-0.0122	16	0.0005	0.0003
12	-0.1852	17	-0.1743	-0.1873
13	-0.1770	18	-0.1587	-0.1321
14	-0.1395	19	-0.1033	-0.1035
15	0.0747	20	0.0517	0.0535
16	0.0388	21	0.0542	0.0537
17	-0.0320	22	0.0018	-0.0015
		23	-0.0024	-0.0026
		24	-0.0046	-0.0045
		25	0.0000	0.0000

Table (Q-XXVII)

Non-planar Frequencies Calculated from the Refined Force Constants

		Set I	Set II	
	Observed	Calculated	Calculated	Calculated
			A	B
PBQ-h_4				
b_{3g}	998	997	997	962
	794	785	792	794
	243	236	242	241
b_{1u}	882	880	882	892
	505	489	506	505
	108	123	118	109
b_{2g}	745	750	747	746
au	969	991	968	970
	310	310	311	308
PBQ-d_4				
b_{3g}	843	853	909	851
	711	669	623	632
	228	232	239	237
b_{1u}	793	796	775	788
	418	394	417	419
	106	121	116	105
b_{2g}	574	582	579	580
au	766	772	765	788
	275	282	277	274
(25)d_2				
b_g	937	936	925	945
	790	790	772	788
	459	438	460	464
	290	293	290	288
	106	122	117	105
au	928	929	951	921
	787	780	777	755
	617	610	596	599
	235	234	240	239
(26)d_2				
b_1	943	943	960	941
	820	822	839	819
	751	735	700	703
	450	430	448	452
	235	234	240	239
	107	122	117	105
a_2	930	918	901	922
	630	631	630	632
	295	296	293	291

Table (Q-XXVII) Cont.

	Observed	Set I	Set II	
		Calculated	Calculated A	Calculated B
PBQ-d_1				
	998	994	986	986
	300	302	300	300
	850	849	852	851
	474	457	475	475
	108	123	108	117
	670	673	661	661
	933	933	931	931
	792	780	778	776
	238	235	240	240

Table (Q-XXVII)

Calculated Non-planar Force Constants for Parabenzoquinone

No.	Description	Set I	Set II	Description	Set III
1	101	0.1344	0.1226	101	0.1192
2	202	0.2720	0.2597	202	0.1754
3	102	-0.0656	-0.0655	102	-0.1095
4	707	0.6548	0.7017	707	0.6890
5	808	0.4507	0.4469	808	0.4408
6	708	-0.1419	-0.1218	708	-0.1333
7	809	-0.1379	-0.1345	809	-0.1265
8	108	-0.1852	-0.1738	108, 209	-0.1671
9	209	-0.1770	-0.1742		
10	310	-0.1395	-0.1365	310	-0.1399
11	109	0.0747	0.0762	109, 608	0.0826
12	608	0.0388	0.0356		
13	210	-0.0320	-0.0333	210	0.0286

Calculated Frequencies

	Observed	Calc. I	Calc. II	Calc. III
$PBQ-d_4$	843	818	834	768
	711	670	670	659
	228	219	230	167
	793	793	802	788
	418	410	409	365
	106	119	122	125
	574	583	583	580
	766	804	800	774
	275	285	280	246
PBQ-h4	998	955	957	760
	794	788	801	928
	243	224	235	167

Table (Q-XXVII) Cont.

Observed	Calc. I	Calc. II	Calc. III
882	873	880	879
505	509	508	449
108	121	124	126
745	751	750	747
969	1021	1018	1002
310	317	311	269

Chapter III.

Table (HQ-I)

Symmetry Classes of the Hydroquinones

	Free Molecule		Solution
	Cis (OH)	trans (OH)	
HQ	C_{2v}	C_{2h}	V_h
2HQ	C_s	C_s	C_s
23HQ	C_{2v}	C_s	C_{2v}
25HQ	C_i	C_{2h}	C_{2h}
26HQ	C_s	C_s	C_{2v}

Hydroquinone

The examination of the spectra of p-hydroquinone and its simple derivates should help one understand the changes which take place in the ring vibrations on going from the quinonoid to the benzenoid form. There is, however, the added complication of hydrogen bonding.

The unit cell in hydroquinone is known to contain four molecules and the (O-H) groups are completely hydrogen bonded. The crystal structures of the chloro-derivatives have not as yet been determined. It is, nevertheless, likely that their lattices will bear some resemblance to that of hydroquinone itself, in that there would be at least two molecules per unit cell and that hydrogen bonding is extensive if not complete. This is expected to give rise to a reduction in the original symmetry of the free molecules and may also produce a splitting of some fundamental absorptions. Table (HQ-I) gives a list of the symmetry point groups to which the hydroquinones considered in this study belong. Planarity of these molecules is assumed, it is known, however, that 2,3:dichloro p-benzoquinone, for example, is slightly non-planar and the possibility that 2,3:dichloro p-hydroquinone might also be non-planar cannot therefore be excluded. In view of the relative uncertainty regarding the exact arrangement of the chloro hydroquinones in their unit cells and hence their local symmetry it may be best to deal with the assignments of the vibrational spectra disregarding symmetry considerations, for the time being.

Hydroquinone and its chloro derivatives are insufficiently soluble in the most convenient organic solvents for spectroscopic work e.g. CCl_4, CS_2. The advantage of their greater solubility in solvents such as $CHCl_3$, CH_3CN is offset by the strong interactions between the solvent and solute molecules which give rise to some considerable changes in the spectra of both solvent and solute. This rules out almost completely any possibility of compensating for solvent absorptions so that one is left with fewer and narrower windows; furthermore when different solvents are used to cover the largest possible frequency range it is found that the changes in the solute spectra depend on the solvent. This obviously renders the whole question of studying the spectra of these compounds in solution somewhat complicated and of doubtful value at this present stage. Nevertheless, it is possible to single out certain absorptions, in the solute spectra, which are not changed or only slightly changed by going from the solid state to solution or from one solvent to another.

The infrared spectra of hydroquinone have been recorded by Prichard[23], but the earliest reference to the Raman frequencies is made by Landolt-Börnstein[13]. Both the infrared and Raman spectra of this compound and some of its chloro derivatives have been dealt with here and a list of suggested assignments are given in table (HQ- II).

4000-2000 cm^{-1} :

This region contains the (O-H) and (C-H) stretching vibrations which give rise to a very broad and intense band having a maximum at 3266 cm^{-1} and a weak absorption at 3030 cm^{-1}. Three weak and broad bands are also observed at 2820, 2690 and 2560 cm^{-1}.

2000-1000 cm^{-1}:

Some of the (C-C) stretching modes are expected to occur in this region. The two bands at 1473 and 1520 cm^{-1} are both assigned to ν(C-C) modes by Prichard, however NCA shows that both of these modes involve a considerable amount of β(O-H) character. This is also clear from the sensitivity of these bands to deuteration. Neither of these bands are observed in the Raman effect. The infrared spectrum of the solid film contains a complex pattern of weak absorptions at 1600 cm^{-1} and 1628 cm^{-1}, the two main bands at these positions are assigned to stretching vibrations. The spectra of the other hydroquinones contain two distinct absorptions in the same region and the corresponding lines in hydroquinone's Raman spectrum occur at 1604 and 1624 cm^{-1}.

The 1356 cm^{-1} band in the infrared spectrum of hydroquinone decreases in intensity on deuteration and a new band appears at 1000 cm^{-1}. The former band may thus be described as mainly β(O-H). The shoulder band at 1334 cm^{-1} is assigned to the remaining ν(C-C) mode.

The spectrum of hydroquinone in the solid phase shows a multiple absorption in the 1250 cm^{-1} range the maxima being at 1260, 1246 and 1212 cm^{-1}. The preferred assignments for this group are β(C-H)

1260 cm^{-1}, ν(C-O)$_s$, 1246 cm^{-1} and ν(C-O)$_{as}$ 1212 cm^{-1}.

The remaining in-plane β(C-H) bands are assigned to the bands at 1169, 1100 and 1012 cm^{-1}. Of these only the first two have corresponding Raman lines at 1166 and 1101 cm^{-1}; both are weak ones. Two extremely weak absorptions are observed around 930 and 912 cm^{-1} in the spectrum of the solid sample, both have been previously assigned to (C-H) out-of-plane bending vibrations together with the bands at 830 and 832 cm^{-1}. The only band observed in the infrared spectrum recorded for this work is the one occuring at 834 cm^{-1}. This is also active in the Raman effect, though much less intensely than the band observed at 854 cm^{-1}, which is completely absent from the infrared spectrum. The most suitable assignment for this line on account of its position and intensity is to a γ(C-H) or a ring breathing mode. The latter mode is assigned in the spectrum of p-difluorobenzene to a band at 858 cm^{-1} and occurs in a similar position in a number of other para-substituted benzene derivatives. Another mode which is expected to give rise to an intense Raman line in the region of 800 cm^{-1} is the highest of the α(C-C-C) modes. The only candidates for this assignment are the lines at 832 and 700 cm^{-1}. The first is probably best allocated to a γ(C-H) deformation and the latter which is also very weakly active in the infrared is provisionally assigned to an out-of-plane (C-C) deformation. This leaves the infrared absorption at 757 cm^{-1} in the solid phase for assignment as an in-plane (C-C) bending mode. No Raman shift is observed around this wavenumber, which could mean that the latter assignment is incorrect; alternative assignments for this region would involve allocating the band at 834 cm^{-1} to the α(C-C-C) mode and the assignment of the infrared absorption at 757 cm^{-1} to a ϕ(C-C) fundamental. This would leave the Raman line at 700 cm^{-1} and the corresponding infrared absorption at 704 cm^{-1} to be assigned to another ϕ(C-C) or a α(C-C-C) mode. The previous set of assignments is nevertheless retained since it is in much better agreement with the assignments for other similar compounds and with the results of the preliminary normal co-ordinate analysis.

The in-plane bending modes β(C-F) in p-difluorobenzene occur at 427 and 350 cm^{-1}. The corresponding value for the symmetric β($C-NH_2$) in p-phenylene diamine is 421 cm^{-1}. Both of the α(C-C-C) modes in parabenzoquinone have been assigned quite unambiguously to the bands at 443 and 408 cm^{-1}. The preferred assignments for the β(C-O) modes in hydroquinone are thus the infrared band at 520 cm^{-1} and the Raman line at 464 cm^{-1}, the former is split, probably by structural or hydrogen bonding factors.

There are three remaining bands at 55, 102, 154 and 195 cm^{-1} in the far infrared spectrum and at 96 and 78 cm^{-1} in the Raman effect. Some of these may be due to vibrations of the lattice or hydrogen bond vibrations. (The spectrum of hydroquinone in the region 2000–3000 cm^{-1} has well resolved features separated by about 130 cm^{-1}).

Table HQ-II

Assignments of the Fundamental Frequencies of the Hydroquinones

		HQ	2HQ	23HQ	25HQ	26HQ
1	ν(C-C)	1624	1609	1604	1618	1612
2	ν(C-C)	1604	1595	1598	1594	1593
3	ν(C-C)	1520	1526	1491	1483	1484
4	ν(C-C)	1473	1460	1453	1437	1442
5	ν(C-C)	1334	1232	1239	1275	1303
6	ν(C-O)	1246	1202	1206	1241	1216
7	ν(C-O)	1212	1202	1196	1202	1216
8	β(C-H)	1260	1282	1260	1226	1329
9	β(C-H)	1169	1170	1111	1183	1178
10	β(C-H) *	1100	1085	1050	1134	1076
11	β(C-H) *	1012	1050	866	1071	848
12	(R-B)	854	859, 785	782	808	815
13	α(C-C-C)	757	827	726	710	795
14	α(C-C-C)	647	684	606	686	595, 504
15	α(C-C-C)	375	458		449, 420	
16	β(C-O)	520	495	534	491	560
17	β(C-O)	464	458		396, 473	
18	γ(C-H)	930	932	951	947	956
19	γ(C-H)	912	912	820	878, 874	858
20	γ(C-H)	832	815			
21	γ(C-H)	811				
22	ϕ(C-C)	704	783	553	580	702
23	ϕ(C-C)		583	477	473, 420	504
24	ϕ(C-C)	375	326		317	
25	γ(C-O)	220	252			
26	γ(C-O)	126	193			

* or (C-Cl)

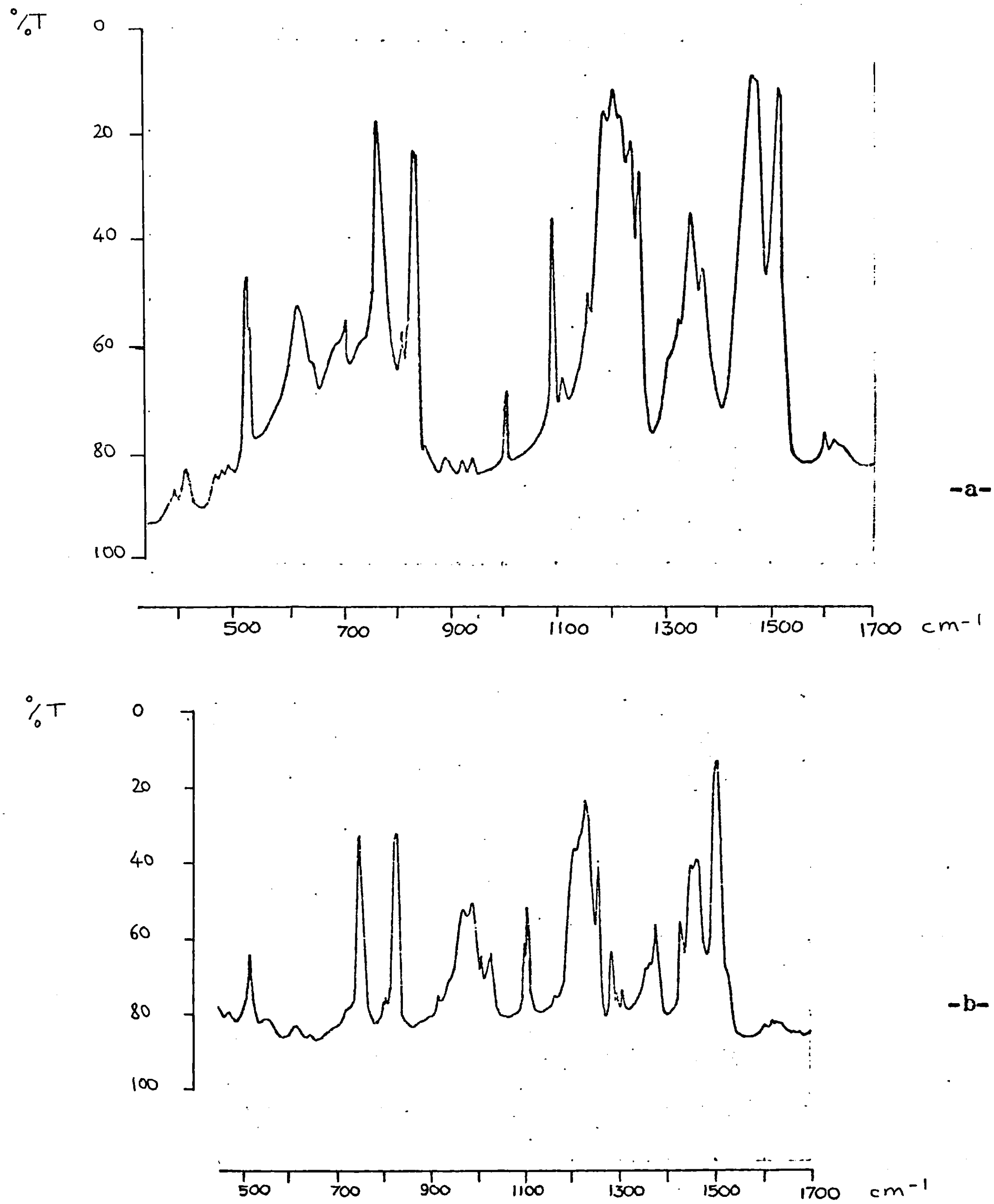
Table (HQ-II) Cont.

(O-H) Stretching and Bending Vibrations of some p-Hydroquinones

	HQ	2HQ	23HQ	25HQ	26HQ
ν(O-H)	3268	3350	3312	3240	3350
ν(O-H)	3288	3250	3312	3240	3250
β(O-H)	1474	1377	1320	1308	1368
β(O-H)	1356	1372	1320	1308, 1183	1368, 1178
γ(O-H)	616, 757	783			613
γ(O-H)	527	544	544	518	560

(C-H) Stretching Vibrations

	HQ	2HQ	23HQ	25HQ	26HQ
ν(C-H)	3060	3068	3070	3050	3074
ν(C-H)	3060	3068	3070	3050	3060
ν(C-H)	3036	3040			
ν(C-H)	3030				



Infrared spectra of (a): parahydroquinone,
(b): very nearly completely deuterated parahydroquinone - $C_6H_4(OD)_2$. (mull spectra).

2:chlorohydroquinone

4000-2000 cm^{-1}

Apart from the extremely broad and intense absorption at 3250 cm^{-1} the only other bands observed in this region are the weak ones at 3060, 3040, 2600 amd 2052 cm^{-1}. The first two are assigned to the (C-H) stretching vibrations and the latter probably arise from hydrogen bonded vibrations.

2000-1000 cm^{-1}

Two very weak absorptions occur at 1863 and 1720 cm^{-1} these may be assigned to combination bands or overtones. The weak-medium bands at 1595 and 1609 cm^{-1} and the medium absorption at 1526 cm^{-1} are assigned to the three highest ν(C-C) modes. A strong and rather broad absorption having a maximum at 1460 cm^{-1} is observed in the solid state spectrum, this absorption is shifted to a slightly higher position in $CHCl_3$ solution and both it and the broad absorption at 1377 cm^{-1} are sensitive to deuteration (under suitable conditions for hydroxyl proton exchange). The former band is assigned to another (C-C) stretching vibration and the latter to the in-plane (O-H) bending mode. This is the most consistent assignment with the behaviour of both bands upon deuteration. However, the spectrum of the partly deuterated and nearly completely deuterated species are not very simply related to the spectra of the non-deuterated compound, this is taken as further evidence of the high degree of mixing between the (C-H)/(O-D) bending modes and the other skeletal vibrations. The highest (C-H) in-plane bending fundamental is assigned to the sharp medium intensity absorption at 1282 cm^{-1}; this appears as an intense line in the Raman effect. The strong infrared absorptions at 1232 cm^{-1} and 1202 cm^{-1} are assigned to ν(C-C) and ν(C-O) vibrations, respectively. The latter band has an ill-defined shoulder absorption on its low wavenumber side. Only one rather weak Raman line is observed in this region and this occurs at 1230 cm^{-1}.

Two more β(C-H) modes are allocated to the medium and weak bands at 1130 and 1085 cm^{-1} and the (C-Cl) stretch is assigned to the band at 1050 cm^{-1}. The NCA treatment shows that the (C-Cl) stretching character is concentrated in this mode and in the three modes, below 1000 cm^{-1}, at 859, 827 and 684 cm^{-1}.

1000-400 cm^{-1}

The (C-H) out-of-plane deformation vibrations are assigned to the infrared absorptions at 932, 912 and 815 cm^{-1}. Only one strong band is observed in the Raman spectrum at 913 cm^{-1}. The infrared spectrum contains ten absorptions in the region 1000-400 cm^{-1} and the Raman spectrum eight lines. Between ten and eleven vibrational modes are expected to give rise to bands in this region, of these three (C-H) out-of-plane bends have been assigned, this leaves three bands above 750 cm^{-1} which may be assigned to a ring breathing mode: 859 cm^{-1}, an in-plane (C-C) bend: 827 cm^{-1}, and an out-of-plane deformation: 783 cm^{-1}.

The weak band at 684 cm^{-1} in the infrared spectrum is allocated to another (C-C) in-plane mode, and the one at 583 cm^{-1} to an out-of-plane

(C-C) vibration, the corresponding Raman line occurs at 560 cm^{-1}. The broad and weak absorption at 544 cm^{-1} is assigned to the (O-H) out-of-plane bending vibrations. The Raman line observed at 495 cm^{-1} is not observed in the infrared it is nevertheless assigned to a (C-O) in-plane bending mode. The fact that this mode is inactive or even weakly active in the infrared is rather surprising in view of its appreciable intensity in other molecules, hence the assignment of the Raman shift is somewhat doubtful. No other band of suitable intensity or position for this assignment in the infrared spectrum is available. It may be that the rather broad and relatively weak absorption at 534 cm^{-1} could constitute an alternative possibility. The data obtained from the Raman spectrum on the region 400-40 cm^{-1} is rather limited by the flourescent nature of the solid sample. A list of preferred assignments for this region is however given in table (HQ-II).

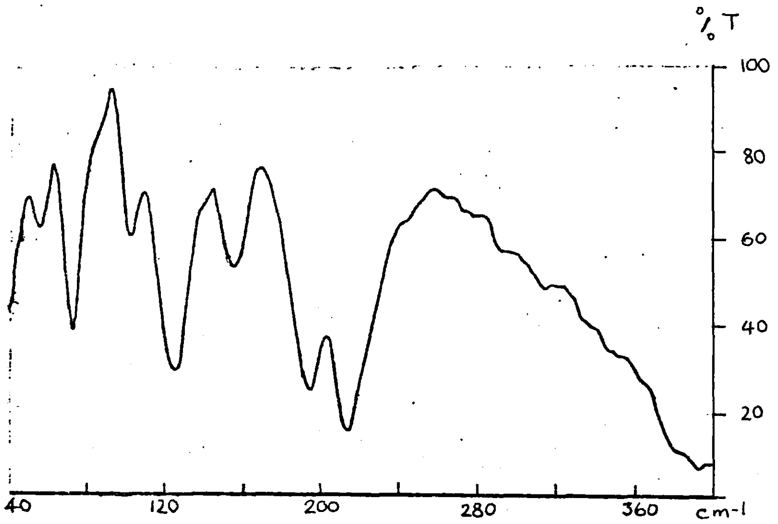
Table (HQ-III)

Observed Spectra of p-Hydroquinone(1) and Chloro p-Hydroquinone(2)

(1)			(2)				
Infrared		Raman	NJ		CH_2Cl_2		Raman
*	I		*	I	*	I	
3268	80		3350	30	3340	M	
3036	5,sh		3250	30,b			
3030	8		3068	5			
2820	11		3040	2			
2690	9		1609	7	1611	w	
2560	5		1595	12	1594	w	
1860	10		1526	25	1509	vs	
1628	5	1624 wm	1474	60,sh			
1608	4	1604 wm	1460	68	1456	m,sh	
		1600 w,sh	1456				
1520	67		1377	35	1334	w	
1506	42,sh		1282	24			1286 w
1480	60		1232	50			1230 vs
1473	45,sh		1202	15	1188	s	
1457	22		1130	12			
1378	37		1085	7			
1356	26		1050	22			
1334	55,sh						
1260	63,sh	1255 s	932	13	930	m	
1246	73		912	28	912		913 s
1212	70,sh		859	30			
1197	21		827	10			
1169	4	1166 m	815	14			
1123	40		809	30			
1100	12	1101 w	781	50			782 s
1012	63		760	13			
930	3		684	5			694 s
912	4		651	2			

Table (HQ-III) Cont.

(1)		(2)		
Infrared	Raman	NJ	CH_2Cl_2	Raman
856	854 vs	583 10		560 w
832 63	832 s	534 66		
811 10		517 5		
757 44				495 s
704 10	700 wm			440 w
	647 vs			336 vw
616 28				252 vw
527 30				242 s
520 33				193 w
	484 mw,sh			110 vs
	472 s			
457 3	462 msh			
414 12				
Far Infrared				
391 vvw(?)	375 vs			
294 s				
214 s	220 m,sh			
194 s	180 vw,sh			
154 m	96 vw, sh			
126 s	78 vw, sh			
102 m				
84 w,sh				
54 m				

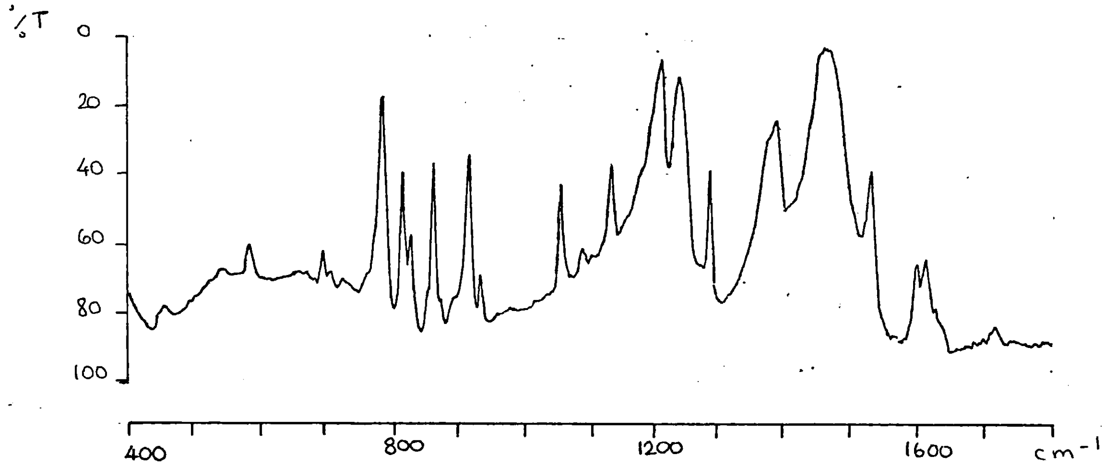


Far infrared spectrum of p-hydroquinone (Wax disc). The spectrum contains instrumental features.

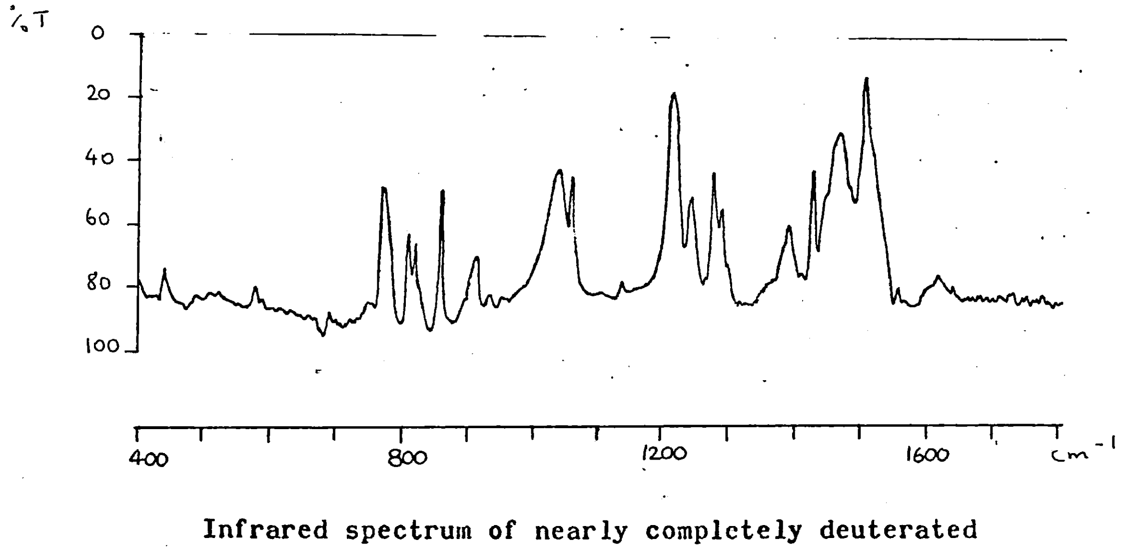
Table (HQ-III) Cont.

Possible Combination Frequencies for 2:Chloro p.Hydroquinones

Observed	Possible Combination	Difference
2600	1377 + 1232 = 2609	9
2052	1595 + 458 = 2053	1
	1460 + 583 = 2043	9
	1377 + 684 = 2061	9
	1232 + 827 = 2059	7
	1232 + 815 = 2047	5
1863	1372 + 495 = 1867	4
	1282 + 583 = 1865	2
	1050 + 815 = 1865	2
	1050 + 811 = 1861	2
	932 x 2 = 1863	1
1720	1526 + 193 = 1719	1
	1232 + 495 = 1727	7
	859 x 2 = 1718	2
	932 + 785 = 1717	3
	912 + 811 = 1723	3
1474	1282 + 193 = 1475	1
	932 + 544 = 1476	2
1456	1202 + 252 = 1454	2
	912 + 544 = 1456	0
1130	932 + 193 = 1125	5
	583 + 544 = 1127	3
684	495 + 193 = 688	4
651	458 + 192 = 651	0
	326 x 2 = 651	1



Infrared spectrum of chloro para-hydroquinone (mull).



Infrared spectrum of nearly completely deuterated sample of chloro para-hydroquinone - p-$C_6H_3Cl\ (DO)_2$.

23:dichlorohydroquinone

4000-2000 cm^{-1}:

The (O-H) stretching vibration gives rise to a very broad absorption having a maximum at 3312 cm^{-1}, the band is not completely symmetric and its intensity decreases more rapidly towards higher wave numbers.. The (C-H) stretching absorptions are obscured by the broad (O-H) absorption but two extremely weak bands are barely visible at 3020 and 3060 cm^{-1}, in the solid phase spectrum. These are possibly due to the (C-H) modes.

2000-1000 cm^{-1}:

The bands at 1604 and 1598 cm^{-1} are assigned to ν(C-C) modes the latter is an ill-defined shoulder absorption and both are of similar intensity. Two more ν(C-C) modes are allocated to the bands at 1491 and 1453 cm^{-1} both are significantly sensitive to deuterium exchange. The broad band at 1350 cm^{-1} is readily assigned to the δ(O-H) mode. This band has a medium intensity shoulder absorption at 1320 cm^{-1} and a weak one at 1289 cm^{-1}, the latter is allocated to a (C-C) stretching vibration and the former which also disappears upon deuteration is attributed to another (O-H) bending vibration. The absorption at 1260 cm^{-1} has a shoulder absorption at about 1250 cm^{-1}. As the compound is progressively deuterated the main band appears to become broader and more intense, the main absorption is allocated to a (C-H) in-plane bend and the absorptions at 1206 and 1196 cm^{-1} are assigned to (C-O) stretches.

The bands which remain to be assigned in this region are expected to arise from (C-H) and (C-Cl) vibrations, two very weak absorptions are observed above 1000 cm^{-1} which might be connected with these fundamentals. The Raman spectrum of this compound in this region is not as useful as was hoped due to the fluorescence shown by the solid. The only intense peak found in the range 2000-1000 cm^{-1} in the Raman spectrum is the one at 1300 cm^{-1}. This is attributed to a (C-C) stretching vibration. Some weak Raman bands are also observed at 1150 and 1200 cm^{-1}. These possibly correspond to the infrared bands at 1195 and 1206 cm^{-1}. The absorptions at 1110 and 1050 cm^{-1} in this spectrum are assigned to a (C-H) bend and a (C-Cl) stretch, both are rather weak in the Raman effect.

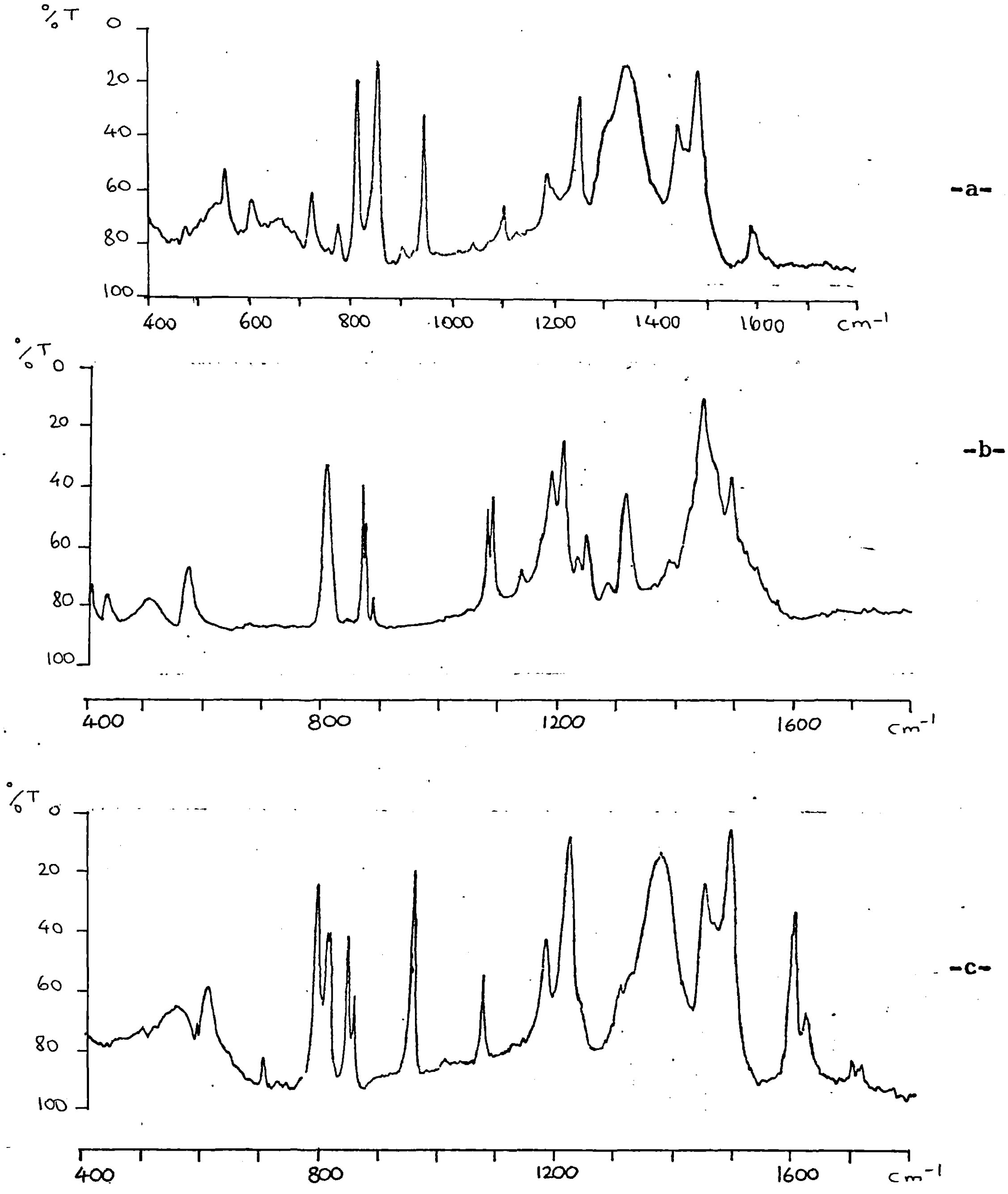
400-1000 cm^{-1}

The remaining (C-Cl) stretch is allocated to the intense band at 866 cm^{-1}. Two intense absorptions are found at 951 and 820 cm^{-1}. These are assigned to out-of-plane (C-H) bends, and the weak bands at 782 and 726 cm^{-1} to the ring breathing mode and an in-plane (C-C) mode. A broad band occurs at 534 cm^{-1}. This is, in effect, a shoulder absorption associated with the more intense band at 553 cm^{-1}, the former absorption disappears upon deuteration while the latter moves to a lower frequency at 544 cm^{-1}. The first absorption is therefore assigned to a γ(O-H) mode and the one at 553 cm^{-1} to a β(C-O) one, or possibly to an out-of-plane (C-C) deformation. The Raman spectrum contains a very intense peak at 558 cm^{-1}. The only other absorption left in this region is the one at 477 cm^{-1} and the most likely assignment for this is an in-plane or ϕ(C-C) deformation.

Table (HQ-IV)

Infrared and Raman spectra of observed spectra of
2,3:Dichloro p-Hydroquinone

NJ		CHBr$_3$		CCl$_4$		Raman (1)		Raman (2)	
*	I	*	I	*	I	*	I	*	I
3312	70,b	3540	(7)						
1604	(10)	1600	(5)			1608	mw		
1598	(14)								
1508	(40)								
1491	(70)	1492	(10)						
1455	(37)	1474	(71)	1479	(38)				
		1437	(4)						
1350	(73)								
1320	(50)								
1289	(10)					1291	s	1292	s
1260	(39)								
1204	(20)	1218	(35)	1220	(38)	1206	vw		
1197	(30)								
1138	(5)								
1112	(15)								
1103	(5)sh								
1051	(6)								
951	(50)	945	(21)			958	ms		
914	(7)					912	vw		
866	(75)	856	(43)	857	(20)	856 852	vw		
820	(75)	817	(31)			817	w		
782	(16)								
762	(3)								
760	(3)								
726	(24)					728			
						696	vw		
606	(14)								
563	(24)	557	(12)	558	(23)	558	s	554	s
534	(24)								
477	(6)								
						464	w,b		
405	(8)b					380	mw		
						336	mw		
						302	w		
						258	m		
						200	m		
						182	s		
						170	s		
						96	vw		



Infrared spectra of

(a) 2,3:dichloro parahydroquinone

(b) 2,5:dichloro parahydroquinone

(c) 2,6:dichloro parahydroquinone

2,5:Dichlorohydroquinone:

The crystal structure of this compound is not known. Complete hydrogen bonding is, however, expected to take place in the solid phase, causing some reduction in the molecular symmetry. Nevertheless, comparison of the Raman and infrared spectra reveals that a number of infrared absorptions are inactive or very weakly active in the Raman effect, and vice versa. It is, therefore, possible that the crystal structure of this molecule allowes the C_{2h} selection rules to be, at least loosely, adhered to.

2000-1000 cm^{-1}

The infrared spectrum contains two exceedingly weak absorptions around 1600-1620 cm^{-1}, the corresponding bands in the Raman spectrum are very much stronger and appear at 1593 and 1618 cm^{-1}. The highest two (C-C) stretches are assigned to the bands that are active in the Raman spectrum. Two more (C-C) stretches are assigned to the intense infrared absorptions at 1483 and 1437 cm^{-1}. The latter is rather sensitive to deuteration and neither seem to give rise to recognisable Raman lines. The region 1300-1400 cm^{-1} is expected to contain the (O-H) in-plane deformation. A broad band is observed at 1308 cm^{-1} which is assigned to both (O-H) modes simultaneously. The β(O-H) and β(C-H) deformations give rise to two doublet lines in the Raman spectrum, which have centres at 1308 and 1295 cm^{-1}, the splitting of the two doublet lines is roughly the same in both cases, and is probably attributable to the crystal lattice structure.

The infrared absorptions in the range 1300-1000 cm^{-1} are due to (C-C), (C-Cl) and (C-O) stretching and to (C-H) bending vibrations. Information on this region from the Raman effect is limited by the intense flourescence shown by this compound. It is possible however, to observe a broad and rather weak line at 1200 cm^{-1}, together with a line at 1064 cm^{-1}. The infrared absorptions in this region may be assigned in a manner consistent with the assignments of its related compounds and with the results of the preliminary NCA treatment. These assignments are shown in table (HQ-II) and do not require any further discussion at the moment.

1000-400 cm^{-1}

The Raman spectrum contains intense, medium and weak lines at 710, 974 and 686 cm^{-1}. None of these is active in the infrared spectrum, which contains three sharp absorptions at 878, 874 and 885 cm^{-1}. The latter is the weakest of the three. In addition to these there is a broad and intense band at 808 cm^{-1}. It is difficult to assign all the Raman and infrared bands to fundamentals, however the infrared absorption at 885 cm^{-1} is a sufficiently weak one to be provisionally assigned to a combination. A combination from which it might arise is : 473 + 420 = 893 cm^{-1}. The bands at 874 and 686 may be assigned to a (C-H) out-of-plane deformation and a (C-Cl) mode respectively. A possible set of assignments for the remaining modes below 1000 cm^{-1} is given in table (HQ-II).

26:Dichlorohydroquinone:

The (O-H) stretching vibrations occur at 3350 and 3250 cm^{-1}. The two bands are not very well resolved and are broad as is usual in this phase. The lower absorption is assigned to the intramolecularly bonded (O-H) vibration. The (C-H) stretching vibrations give rise to the extremely weak absorptions at 3074 and 3060 cm^{-1}.

2000-1000 cm^{-1}

The weak and moderately intense bands at 1612 and 1593 cm^{-1} are assigned to (C-C) stretching modes. The latter has a resolved shoulder peak at 1589 cm^{-1} which probably arises from the crystal structure. The main band at 1593 cm^{-1} is more intense than its counterpart in the spectra of the other hydroquinones but it does, however, resemble very closely in its intensity and structure the corresponding absorption of 2,6:dichloro p-aminophenol hydrochloride, at 1573 cm^{-1}.

The bands at 1484 and 1442 cm^{-1} are also assigned to (C-C) stretching modes; the corresponding assignments for the aminophenol are 1487 and 1434 cm^{-1}. The final (C-C) stretching vibration is provisionally allocated to the band at 1303 cm^{-1} in the infrared spectrum. This together with the (O-H) deformation vibration which is assigned to the broad absorption at 1368 cm^{-1} appear to contain a considerable contribution from the β(C-H) mode. The region 1000-1300 cm^{-1} is supposed to contain the (C-O) stretches, ν(C-Cl) and β(C-H) modes. A very intense absorption is observed at 1216 cm^{-1} which may be allocated to one of the (C-O) fundamentals, if the second, possibly antisymmetric (C-O) stretch is assigned to the band at 1178 cm^{-1} then one is left with only one absorption at 1073 cm^{-1} for assignment to ν(C-Cl) and β(C-H) modes, which is a somewhat unsatisfactory situation. Alternatively one would have to seek the second ν(C-O) mode beyond 1300 cm^{-1}, or assume a coincidence at 1216 cm^{-1} of both the symmetric and anti-symmetric ν(C-O) modes. The absorption at 1073 cm^{-1} may then by assigned to a (C-Cl) stretch and the one at 1178 cm^{-1} to a β(C-H) vibration. The preliminary NCA treatment shows a very small amount of (C-Cl) stretching character to be associated with the higher band at 1178 cm^{-1} and reveals that certain modes below 1000 cm^{-1} contain a substantial amount of (C-Cl) stretching character.

1000-400 cm^{-1}

The (C-Cl) stretching mode expected in this region is possibly best assigned to the band at 848 cm^{-1}, while the medium intensity shoulder peak at 858 cm^{-1} is allocated to a γ(C-H) mode. Another out-of-plane (C-H) deformation is assigned to the intense band at 956 cm^{-1}. The medium-strong doublet absorption at 815 cm^{-1} is allocated to the ring breathing mode and the intense one at 795 cm^{-1} to an in-plane (C-C) bend. A weak band occurs at 702 cm^{-1} which may be assigned to an out-of-plane (C-C) deformation. The remaining assignments for this region are listed in table(HQ-II) together with those for the higher fundamentals active in the infrared spectrum.

Table (HQ-V)

Observed spectra of 2,5:Dichloro p-Hydroquinone (1) and
2,6:Dichloro p-Hydroquinone (2)

(1)		(2)	
Infrared	Raman	Infrared	Raman
* I		* I	
	1618 wm	3350 (65)	
	1604 wb	3250 (60)	
	1594 wb		
1483 (44)		3074 (2)?	
1437 (62)		3060 (2)?	
1308 (30)	1306} md	1612 (20)	
	1309}	1593 (52)	
1275 (7)	1296} md	1589 (45)	
1241 (21)	1294}	1484 (84)	
1226 (15)		1472 (55)	
1202 (50)	1200 wb	1442 (67)	
1183 (35)		1368 (75)	
1131 (9)		1303 (20)	1310 m
1084 (30)		1216 (70)	
1076 (28)		1178 (39)	
	974 m	1073 (28)	
885 (12)		956 (60)	952 s
874 (30)		858 (30)	
818 (42)		817} (50)	
808 (51)		813} (50)d	
	710 vs	795 (66)	
580 (20)		706 (10)	
518 (8)b		613 (28)	
449 (9)	491 w	560 (10)b	
420 (12)	473 sm	504 (3)	510 s
	396 wsh	456 (1)?	
	328 w		374 s
	317 vs		284 wm
	252 wsh		244 wm
	241 vs		226 vs
	180 wsh		210 m
	166 vw		
	160 mw		
	80 d		
	70		
	50		

b = broad
d = doublet

Hydroquinone Planar Frequency Calculations:

The planar vibrations of the hydroquinones were calculated using a number of trial sets of the two major types discussed in the case of the quinone calculations - i.e. with and without discrimination between interaction terms arising from (C-O) and (C-H) bending co-ordinates. Examples of these force constant sets are given in tables (HQ - VI, VII), together with the corresponding values of the quantities:

$$\sum_{i}^{N-3} \Delta\nu_i / N-3 \quad , \quad \sum_{i}^{N-3} \Delta\nu_i / \nu_i$$

As was found with the calculations of the planar and indeed non-planar vibrations of the aminophenols; the fact that one is relatively ignorant of the interaction parameters between the (C-O-H) bending and other internal co-ordinates leads to considerable uncertainty regarding the force constants arrived at by any refinement process.

The planar vibrations of the chlorohydroquinones were calculated using the (C-Cl) stretching and bending parameters utilised in the chloroquinone calculations. Examples of the results obtained for hydroquinone and 2:chlorohydroquinone are given in tables (HQ-VIII, IX).

Hydroquinone Non-planar Frequency Calculations:

The force field parameters given in table (HQ-X) have been used in calculating sets of preliminary frequency values, which are listed in table (HQ-XI). As in the cases of the diazo-oxides and aminophenol molecules, the main source of uncertainty involving this calculation is the choice of diagonal and non-diagonal constants for the additional fragment (O-H), (N-N), (N-H) and (O-H) respectively. As the first approximation, the non-diagonal constants involved in (O-H) deformation motion are assumed to be equal to zero in calculating the frequencies given in table (HQ- XI), while the diagonal constants are assumed to be roughly equal to the ϕ(C-C) parameter rather than to the γ(C-H) constant since the γ(O-H) deformation is in fact more of a torsional motion.

The calculation was carried out using a number of values for the force constant γ(O-H) in the range 0.40 - 0.20 x 10^{-11} erg rad^{-2} The cartesian displacement figures, and potential energy distribution reveal that considerable mixing takes place between the (C-C) and (O-H) deformation vibrations despite the fact that all the interaction constants involving γ(O-H) are set to zero. This mixing is found to occur for values throughout the range mentioned above although additional interaction between (O-H) deformation and (C-H) bending is introduced for the higher values. The frequencies having the largest contribution from (C-O) vibrations are those within the range 200 - 400 cm^{-1}, and the calculated (C-Cl) deformation vibrations have values in the region 200 - 100 cm^{-1}.

Regarding the lowest ϕ(C-C) torsional motion the same observation is made in the case of the hydroquinones calculated frequencies as in the cases of the quinones aminophenols and diazo-oxides, which is that the modes containing substantial contributions from diagonal force constants labelled 1,2, and 3 in table (HQ- X), include one occuring in the region 200 - 240 cm^{-1}. This behaviour is also noted in the case of p-dichlorobenzene whose non-planar frequencies have been calculated using Scherer's force field, it is therefore not surprising to find that similar behaviour is exhibited by the results on the calculations on the above mentioned compounds.

Tables (HQ- XII and XIII) contain a summary of the effect of altering the γ(O-H) force constants upon the calculated frequencies and potential energy distribution, in the case of 2,5:dichloro-p-hydroquinone. The force field used in these calculations is that of 1,2,4,5:tetrachlorobenzene, with the γ(O-H) non-diagonal force constants equal to zero and the diagonal γ(O-H) equal to 0.3x10^{-11} erg rad^{-2}. The agreement between the calculated and observed frequencies is not satisfactory, this is possibly, at least partly, due to the fact that the large magnitude of the ϕ(C-C) force constant :

is inadmissible in the case of this molecule unlike the situation in the comparable bond

in the case of 1,2,4,5:tetrachlorobenzene.

A simple Valence Force Field for planar Hydroquinone Vibrations.

Table (HQ- VI)

Sets -A-

Serial No.	Description	I	II	III
1	101	2.0305	2.0584	2.0584
2	102	0.3400	0.3030	0.2922
3	108	-0.1057	-0.1057	-0.1057
4	213	-0.2890	-0.4017	-0.4057
5	119	-0.3166	-0.5698	-0.6243
6	707	1.8365	1.2826	1.2826
7	808	1.0174	1.0174	1.0174
8	708	-0.2934	-0.2698	-0.2698
9	709	-0.1715	-0.0287	-0.0071
10	710	0.0943	0.0591	0.0663
11	713	-0.2545	-0.1736	-0.1476
12	714	-0.0225	-0.0192	-0.0330
13	819	-0.2901	-0.3723	-0.4124
14	1222	-0.0847	0.0957	0.0955
15	1313	5.8000	5.6678	5.6658
16	1414	5.8800	5.6678	5.7046
17	1314	0.8595	0.8736	0.8736
18	1315	-0.6133	0.8485	0.4413
19	1316	-0.0479	-0.0117	-0.0117
20	1317	-0.0117	0.2586	0.2370
21	1318	0.2679	0.5050	0.5836
22	1310	0.8467	0.6189	0.6623
23	1322	0.1711	-0.1259	-0.1561
24	1417	0.9910	0.5853	0.4948
25	1419	-0.1787	-0.2881	-0.3122
26	1919	6.7762	6.7100	6.7334
27	2020	5.0930	5.0320	5.0318

Table (HQ- VI)(Cont.)

Sets-A-

28	2021	0.0250	0.0254	0.0031
29	2024	-0.0400	-0.0586	-0.0529
30	2023	0.0080	0.0080	0.0080
31	2525	5.7066	5.8853	5.8854
32	2727	0.8342	0.9421	0.9573
33	2227	0.0000	0.0000	-0.0430
34	1327	-0.0900	0.0000	-0.0155
35	1427	-0.0200	0.0000	-0.0498
$(\sum_i \Delta\nu_i)/N-3$		28.4	9.4	5.2
$\sum_i \Delta\nu_i/\nu_i$		0.748	0.233	0.101

Sets-B-

Table (HQ- VII)

A set of Force Field Parameters used in calculating the Planar Vibrations of p-Hydroquinone.

No.	Description	
1	101	2.3000
2	202	2.3000
3	102	0.2929
4	208	0.0000
5	209	-0.1057
6	608	0.0000
7	107	0.0000
8	207	0.0000
9	307	0.0000
10	119	-0.5697
11	219	0.4758
12	113	-0.4017
13	213	0.0000
14	114	0.0000
15	218	0.0000
16	707	1.2826
17	810	0.0591
18	708	-0.2698
19	709	-0.0287
20	713	-0.1736
21	714	-0.0192
22	808	1.0371
23	809	-0.2698
24	812	-0.0287
25	811	0.0591
26	819	-0.3723
27	822	-0.0953
28	814	0.1736
29	813	0.1736
30	818	-0.0192
31	1313	6.2000
32	1414	0.2000
33	1314	0.8733
34	1318	0.5050
35	1315	0.8484
36	1418	0.2586
37	1316	-0.0117
38	1417	0.5852
39	1319	0.6189
40	1419	-0.2881
41	1322	-0.1258
42	1919	6.6141
43	1922	0.0000
44	2020	5.0320
45	2021	0.0038
46	2024	-0.0586
47	2023	0.0080
48	2525	5.8853
49	2727	0.9585
50	2227	-0.1200
51	1327	0.0000
52	1427	0.0000

Table HQ-VIII

Calculated Planar Vibration Frequencies of p-Hydroquinone (HQ) and Chloro p-Hydroquinone (2HQ)

(Set A(I))

	HQ			2HQ	
Obs.	Diff.	Calc.	Obs.	Diff.	Calc.
1624	18	1642	1609	11	1620
1604	20	1624	1595	8	1587
1520	71	1591	1526	22	1504
1473	4	1477	1460	5	1455
1471	3	1474	1377	23	1400
1358	25	1381	1372	2	1370
1336	13	1321	1232	64	1296
1260	49	1309	1202	45	1247
1246	7	1239	1202	6	1196
1212	11	1223	1282	114	1168
1168	22	1190	1130	47	1083
1100	12	1088	1085	67	1018
1012	70	942	1050	188	862
854	18	836	859	115	744
756	48	708	827	124	693
647	14	561	684	161	523
375	45	420	495	14	481
520	150	370	458	35	423
464	250	259	458	177	281
	$\sum \Delta\nu_i = 748$		242	59	183
				$\sum \Delta\nu_i = 1297$	

Table (HQ- IX)

Calculated Planar Frequencies of p-Hydroquinone (Set-B-)

	Calc.	Obs.
1	3250	3268
2	3250	3268
3	3069	3060
4	3062	3060
5	3036	3036
6	3028	3030
7	1639	1624
8	1605	1604
9	1581	1520
10	1507	1479
11	1457	1471
12	1400	1358
13	1336	1334
14	1310	1260
15	1245	1246
16	1224	1212
17	1186	1169
18	1104	1098
19	1033	1012
20	848	854
21	788	757
22	697	647
23	507	375
24	366	520
25	257	464

Table (HQ - X)

Non-planar Force Constants for 2,6:Dichlorohydroquinone*

No.	Description		No.	Description	
1	101	0.2352	18	811	-0.0048
2	202	0.2352	19	911	0.0167
3	303	0.2352	20	108	-0.1537
4	102	-0.0478	21	209	-0.1537
5	103	0.0000	22	310	-0.1707
6	104	0.0000	23	109	0.0271
7	205	-0.0461	24	608	0.0271
8	707	0.6310	25	210	0.0541
9	808	0.4378	26	211	0.0000
10	909	0.4378	27	110	0.0000
11	708	-0.1103	28	1313	0.4000
12	910	-0.1103	29	1013	0.0000
13	709	0.0060	30	313	0.0000
14	810	0.0060	31	413	0.0000
15	710	-0.0192	32	213	0.0000
16	809	0.0167	33	513	0.0000
17	812	-0.0700			

* The force constants of the 2,6:dichloro derivative were chosen to illustrate the type of (C-Cl) diagonal and non-diagonal parameters used in the calculation of the non-planar vibrations of the chlorohydroquinones.

Table (HQ- XI)

Calculated Out-of-plane Vibrations of some p-hydroquinones

HQ	*	2HQ		23HQ		25HQ +	26HQ+
956	2	945	2	938	2	923	962
931	2	941	2	854	2	922	931
892	2,1	902	2	685	1,3,4	713	701
804	2,1	751	1,2	677	1,2	690	676
691	1,2,3	685	1,3,2	553	3	643	658
652	1,2,3,4	641	4,3	545	4,3	545	567
582	3,4,1	557	3,4,1	399	4,3	378	417
488	4,3	345	4,3	318	3,4	355	341
325	4,3,1	329	4,3,1	222	3,4,5	241	183
237	3	166	3	130	5	146	154
135	3,4	127	5	89	5,3	85	102

* These figures indicate contributions by the coordinates designated:

1: γ(O-H); 2: γ(C-H); 3: ring deformation; 4: γ(C-O); 5: γ(C-Cl).

+: The contributions for these frequencies are similar to those of 2,3:Dichloroparahydroquinone (23:HQ).

Table (HQ- XII)

Variation of the Frequencies and Potential Energy Distribution for 2,5:Dichloro p-Hydroquinone as a Function of f [γ (O-H)]

f [γ (O-H)]

Number	0.400	PED	0.350	PED	0.250	PED
1	879	0.156	909	0.228	896	0.024
2	939	0.553	855	0.528	759	0.758
3	652	0.053	648	0.090	627	0.393
4	453	0.004	453	0.006	452	0.017
5	154	0.003	154	0.004	154	0.007
6	92	0.000	92	0.000	92	0.001
7	983	0.205	971	0.092	963	0.026
8	896	0.475	856	0.593	710	0.994
9	783	0.054	777	0.150	803	0.126
10	380	0.014	379	0.020	377	0.046
11	252	0.002	252	0.003	251	0.007

Table (HQ- XIII)

Variation of the Non-planar Frequencies of 2,5:Dichloro p-hydroquinone as a Function of some Non-diagonal Force Constants

No.	f (O-H)/ (C-C)^{o}		f (O-H)/ (C-C)^{m}	
	0.050	-0.050	0.050	-0.050
1	910	893	924	893
2	793	829	782	846
3	654	626	662	612
4	442	453	420	439
5	154	153	154	151
6	91	92	90	91
7	966	966	966	966
8	819	819	819	819
9	758	758	758	758
10	378	378	378	378
11	251	251	251	251

Chapter IV.

Table (DO - I)

Symmetry Properties of the Diazo-oxides

	Planar Modes	Non-planar Modes
1,4:Benzenediazo-oxide	$12a_1 + 11b_2$	$7a_2 + 3b_1$
2:Chloro 1,4:Benzenediazo-oxide	23 a'	10 a"
3:Chloro 1,4:Benzenediazo-oxide	23 a'	10 a"
2,3:Dichloro 1,4:Benzenediazo-oxide	23 a'	10 a"
2,5:Dichloro 1,4:Benzenediazo-oxide	23 a'	10 a"
2,6:Dichloro 1,4:Benzenediazo-oxide	$12a_1 + 11b_2$	$7a_2 + 3b_1$

Parabenzenediazo-oxide:

4000-2000 cm^{-1}:

The weak bands at 3070 and 3040 cm^{-1} are assigned to the (C-H) modes, and the intense absorption at 2100 cm^{-1} in the solid state spectrum and 2105 cm^{-1} in the chloroform solution spectrum to the ν(C-N-N), or mainly ν(N-N), stretching vibration.

2000-1000 cm^{-1}:

The (C-O) stretching modes in p-benzoquinone have been assigned to the absorptions at 1686 and 1667 cm^{-1}. The highest absorption in this region in the spectrum of the diazo-oxide occurs at 1588 cm^{-1}. This is a broad and intense band with shoulder absorptions at 1605 and 1612 cm^{-1} in the solution spectra. The band at 1588 cm^{-1} is assigned to the ν(C-O) mode and the two shoulder absorptions to (C-C) stretching vibrations. The very much lower value of the (C-O) stretching frequency is not unexpected in view of the possible conjugation between the (C-O) and (C-N-N) fragments across the ring.

A medium intensity absorption occurs at 1398 cm^{-1} in the spectrum of the solid film, it is assigned to another (C-C) mode. It possibly corresponds to the benzoquinone, b_{1u}. mode at 1357 cm^{-1}. This mode is seen to contain a certain amount of (C-N) stretching and (C-H) bending character vibrations, from the NCA carried out using a quinone type force field, (Table DO-XIII). The (C-N) stretching absorption is expected to occur in the range 1200-1500 cm^{-1}. It is also expected to give rise to a rather intense absorption. The CDF obtained from the above mentioned force field show that the (C-N) stretching vibration is delocalised over a number of normal modes.

The modes which possess the highest percentage of (C-N) stretching motion have wavenumbers 1627, 1541, 1258 and 986 cm^{-1}. The first, second and third contain a higher percentage of ν(C-C) and ν(C-O) vibrations. The ν(C-N) mode is therefore provisionally assigned to the absorption at 1245 cm^{-1} in the spectrum of the chloroform solution.

The assignment of the ν(C-N-N) mode to this medium-weak intensity absorption does not seem entirely satisfactory, also on account of its relatively low position. A possible alternative is the equally intense absorption at 1398 cm^{-1}. However, in addition to the higher (C-N) stretching character associated with the low wavenumber band at 1265 cm^{-1} there is its greater sensitivity to the phase change; solution to solid, to support the current assignment.

The weak bands observed at 1315 cm^{-1} and 1220 cm^{-1} are assigned to b_2,ν(C-C) modes. The a_1 β(C-H) modes occur in the spectrum of p-benzoquinone at 1149 and 944 cm^{-1}; the intense band observed at 1145 cm^{-1} in the spectrum of the diazo-oxide is assigned to one of these modes. Two rather weak absorptions occur at 978 and 950 cm^{-1} in the spectrum of the solid state and solution spectra. The second, a_1 β(C-H) bend might be assigned to the higher band alternatively the medium-weak shoulder band at 1110 cm^{-1} might be tentatively chosen for this mode.

The b_2 β(C-H) bending modes of p-benzoquinone are found at 1360 and 1066 cm^{-1}.

The corresponding diazide modes are allocated to the medium shoulder absorption at 1387 and the weak band at 1095 cm^{-1} in the spectrum of the solid.

1000-400 cm^{-1}:

The ring bending mode and, a_1,α(C-C-C) modes are allocated to the absorptions at 775, 720 and 446 cm^{-1}. The corresponding quinone values are 770 and 728, 446 cm^{-1}. The, b_2 (C-C) bending mode is assigned to the medium intensity absorption at 690 cm^{-1}. The planar modes expected in this region are (C-N-N) and (C-O) bends. The first is allocated to the relatively intense absorption at 500 cm^{-1} in the chloroform solution spectrum. The NCA which uses the force field parameters given in table (DO-XIII), predicts a value of 810 cm^{-1} for this mode. The actual position is probably lower. The (C-O) mode is assigned to the absorption at 415 cm^{-1}, in accordance with the corresponding assignments for other quinones and diazo-oxides.

The (C-H) non-planar modes are expected around 958, 882, 993 and 745 cm^{-1} from the experimental values for parabenzoquinone and the calculated wavenumbers. Two of these modes are expected to be infrared inactive. The weak bands at 978, 950, 810 and the intense absorption at 844 cm^{-1} are assigned to these modes as shown in table (DO-VIII). The absorption at 770 cm^{-1} possibly corresponds to the b_{3g} (C-C) mode of parabenzoquinone observed at 795 cm^{-1}. The remaining two deformations of quinone occur at 505 and 402 cm^{-1}. The bends at 630 and 426 cm^{-1} are allocated to these vibrations.

The remaining modes of p-benzenediazo-oxide occur outside the spectral range considered in this study.

3:Chloroparabenzenediazo-oxide:

4000-2000 cm^{-1}:

A weak absorption is observed at 3075 cm^{-1} in the solid state spectrum, this is assigned to the (C-H) stretching vibrations. The only other absorption in this region is the (C-N-N) stretching vibration which occurs at 2116 cm^{-1} in the solid and 2103 cm^{-1} in $CHBr_3$ solution.

2000-1000 cm^{-1}:

The solid state spectrum contains one broad band at 1600 cm^{-1} with two shoulder absorptions at 1625 and 1550 cm^{-1}. The solution spectrum also has a broad band in the same position and has a shoulder band at 1548 cm^{-1}. The Raman spectrum on the other hand has two distinct absorptions a weak one at 1618 cm^{-1} and an extremely intense one at 1584 cm^{-1}. At least two (C-C) stretches are expected in this region in addition to these there is a (C-O) stretch which should occur around 1600 cm^{-1}. The latter is assigned to the main absorption at 1594 cm^{-1} in the solution spectra and 1584 in the Raman and the ν(C-C) vibrations are allocated to the infrared absorptions at 1625 and 1550 cm^{-1}. The latter band is not observed in the Raman spectrum. The shoulder band occuring at about 1520 cm^{-1} in the solid and solution infrared spectra is observed in the Raman spectrum of the solid as an extremely weak band. It is possible that this may be due to a fundamental vibration in which case it is most likely to be a (C-C) stretching mode; only two such vibrations are expected in this region however, and both have been assigned, in a way that is supported by comparison with the spectra of other similar compounds and the results of preliminary NCA using the diazo-oxide force field.

The medium-intensity band observed at 1450 cm^{-1} in the solid and solution infrared spectra is not observed in the Raman spectrum. Its position and intensity are consistent with its assignment as mainly due to a (C-C) stretching vibration possibly mixed with a good deal of (C-H) bending.

The absorption at 1380 cm^{-1} has medium-strong intensity in the infrared spectra and low intensity in the Raman. This is probably a (C-H) bending vibration principally. Another (C-C) vibration is assigned to the absorption at 1270 cm^{-1} which has medium-low intensity in the infrared and Raman spectrum. The bands at 1234 and 1195 cm^{-1} have medium and low intensities in the infrared spectra but the latter is not observed in the Raman spectrum. Both appear, from the NCA, to have a fair contribution from (C-N) and (C-C) stretching motion and (C-H) bending. The first is assigned as a (C-N) stretch and the second as a (C-C) stretching vibration.

The remaining three absorptions in this region are assigned as two (C-H) bends (1121 and 1105 cm^{-1}) and a (C-Cl) stretch at 1019 cm^{-1} both this mode and the one at 854 cm^{-1} appear, from CDF and PED, to involve contributions from ν(C-Cl), β(C-H) and ν(C-C).

The first two appear in the first spectrum of the solid sample but only one band at 1129 cm^{-1} is observed in the Raman spectrum. The band assigned as a ν(C-Cl) absorption is however observed in the Raman and infrared spectra.

1000-400 cm^{-1}:

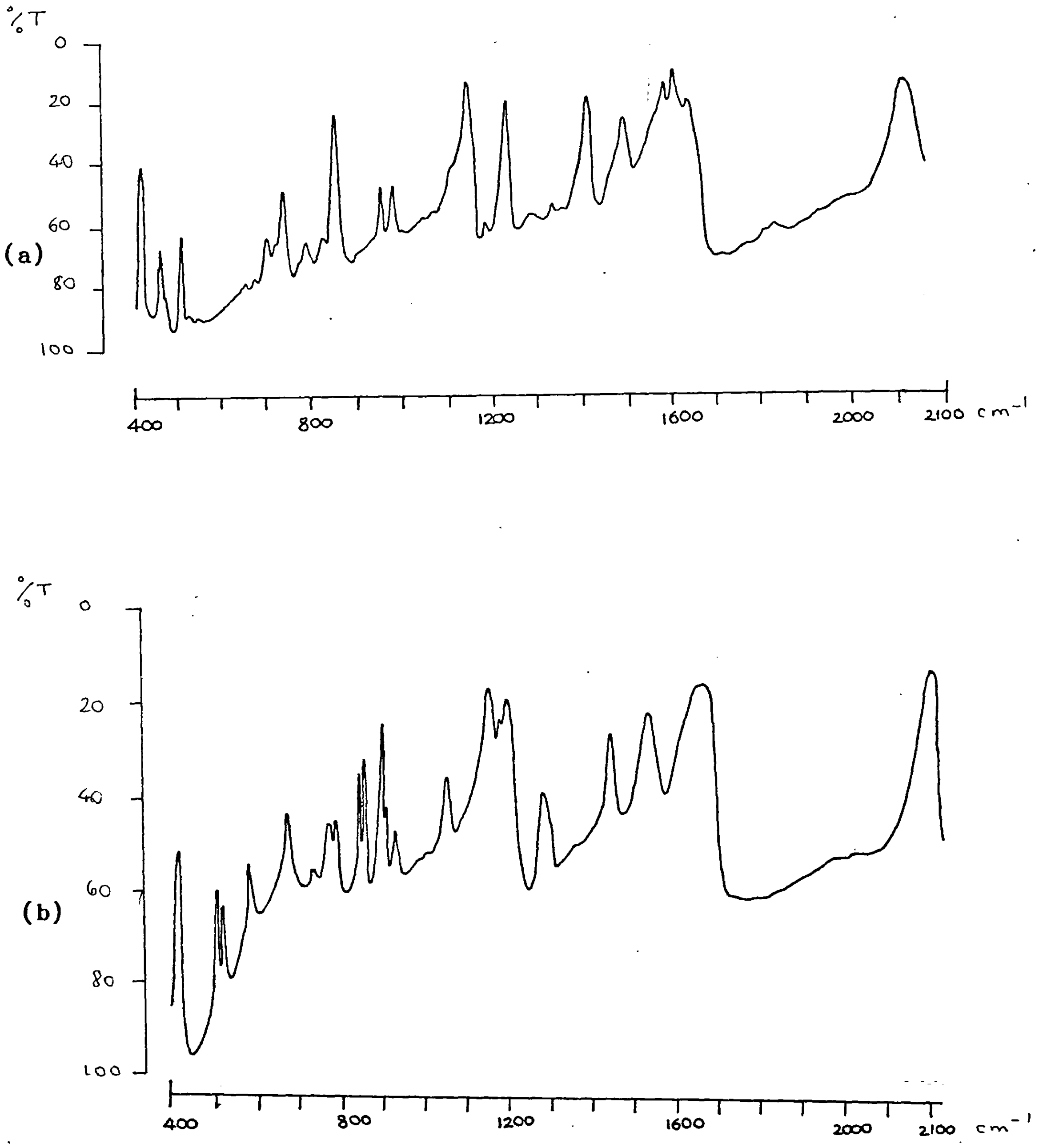
The first absorption in this region occurs at 967 and 970 cm^{-1} in the solid and solution infrared spectra respectively, and at 978 cm^{-1} in the Raman spectrum it is a medium-weak absorption in all these spectra and it is assigned as a (C-H) out-of-plane deformation. The band at 854 cm^{-1} is assigned to the ring breathing mode this fundamental contains a large contribution from (C-Cl) stretching and β(C-N-N) bending as is shown by the NCA. The absorptions at 869 and 803 cm^{-1} are assigned to the remaining two out-of-plane (C-H) deformations. The strong infrared absorption observed at 726 cm^{-1} is assigned to an in-plane (C-C-C) bend. The intensity of this absorption decreases in the Raman spectrum. Another in-plane ring deformation is assigned to the band at 693 cm^{-1} in the infrared. The absorptions at 680 and 598 cm^{-1} are allocated to (C-C) out-of-plane deformations. The first of these two bands appear as a doublet in the infrared spectrum of the solid but only one line is observed at 682 cm^{-1} in the Raman spectrum. The band at 567 cm^{-1} in the solid spectrum is completely absent from the solution spectrum but occurs as an exceedingly weak band in the Raman. This is probably a combination tone (e.g. 380 + 188 = 568 cm^{-1}). The intense absorption at 487 cm^{-1} in the solid state spectrum appears as a strong-medium line in the Raman this is assigned as an out-of-plane (C-N-N) deformation. The band at 430 cm^{-1} in the Raman spectrum is far stronger than its infrared counterpart. It has an associated absorption at 415 cm^{-1} in the solid. These two absorptions are assigned to (C-C) and (C-N-N) in-plane vibrations.

The assignments of the remaining modes in this region are listed in table (DO-VIII).

Observed spectra of Parabenzene diazo-oxide.

Table (DO-II)

NJ	$CHCl_3$	CH_2Cl_2	$(CH_3)_2CO$
* Ɨ			
3070 (1)			
3040 (1)			
3010 (0.7)			
2100 (43)	2105 (71)	2102 (57)	
1610 (39) sh	1612 (65)	1612 (58)	
	1605 (66)		
1580 (45) b	1588 (62) sh	1587 (55)	
1551 (40) sh			
1398 (23)	1400 (18)	1396 (14)	
1387 (14) sh			
1315 (4)			
1265 (5) b	1245 (13)		
1220 (30)			
1145 (32)	1145 (37)	1145 (30)	
1110 (10) sh			
1095 (8) sh	1099 (7)		
978 (10)	978 (2)		
950 (11)	935 (2)		
844 (31)	851 (26)		
810 (4)			
775 (4)			
770 (18)			
720 (7)			
707 (3) sh			
690 (9) sh	630 (2)		690 (4.0)
502 (20)	500 (4)	500 (3)	
462 (9) sh	455 (7)	455 (5)	458 (3.0)
450 (16)			
446 (12) sh			441 (3.0)
411 (25)	415 (22)	415 (18)	406 (4.0)



Infrared spectra of (a): parabenzene diazo-oxide.
(b): 2,6:Dichloro parabenzene diazo-oxide.
(mull spectra).

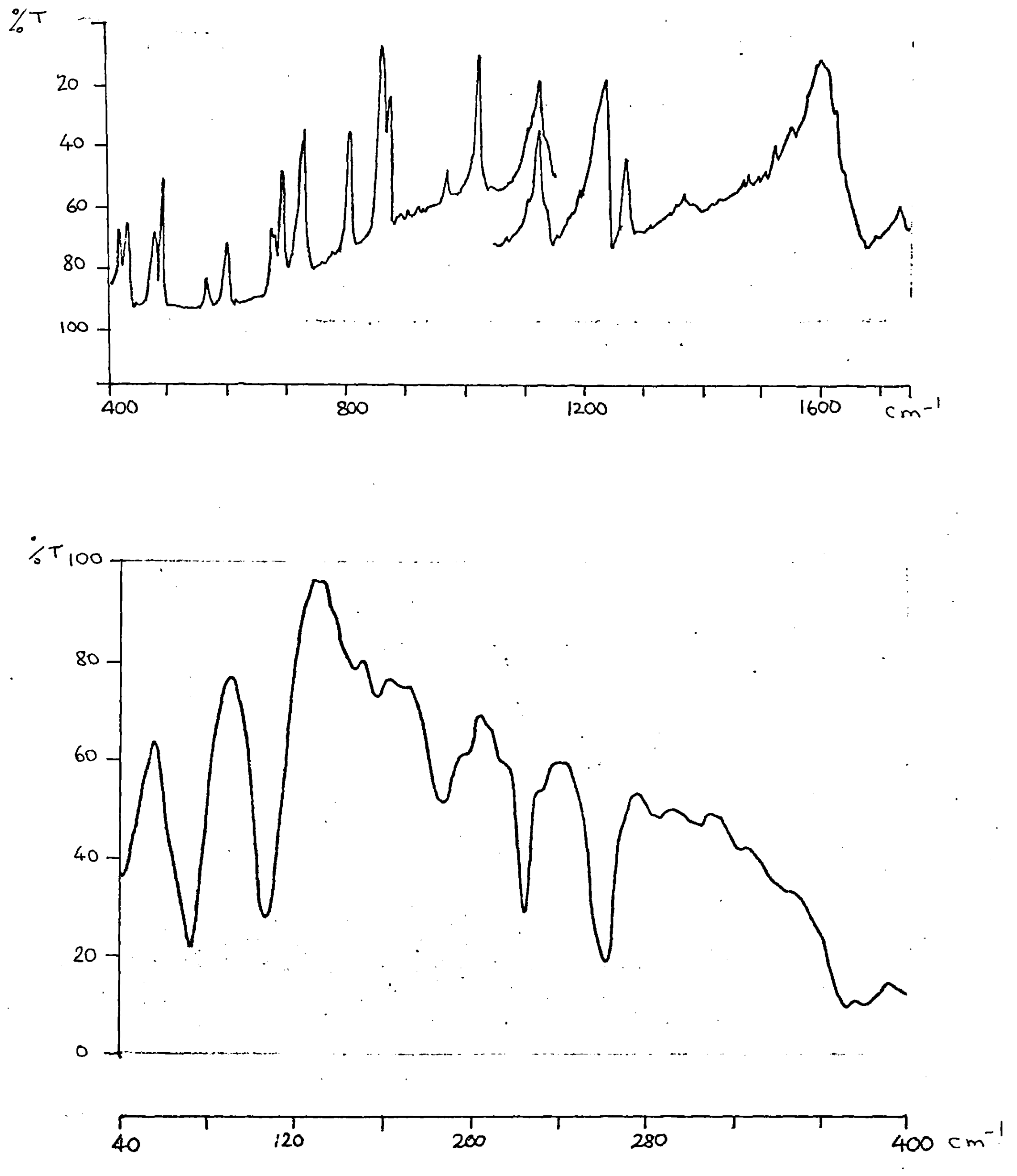
Observed Spectra of 3:Chloroparabenzene Diazo-oxide

Table DO (III)

NJ	Raman	$CHBr_3$
* I		
3075 (90)		
2116 (20)		2103
1625 (50)	1618 mw	
1600 (60)	1584 vvs	1594 (75) b
1550 (40)		1548 (40) sh
1521 (10)	1520 vw	1526 (19) sh
1450 (38)		1445 (38)
1380 (29)	1390 vw	1380 (41)
1270 (29)	1272 mw	1270 (8)
1234 (53)	1231 wm	1237 (55)
1195 (18)	1225	
1121 (37)	1124 sm	
1105 (14)		
		1039
		1037
1019 (41)	1020 s	1021

Table (DO-III)(Cont.)

NJ		R	CHBr$_3$	Far Infrared
*	I			
967	(10)	978 mw	970 (7)	
869	(42)	872 mw		
854	(64)			
803	(37)			
726	(46)	730 mw		
693	(30)			
680	(20)	682 sm		
676	(22)			
598	(20)	601 w		
567	(9)	572 ww	568 (5)	
487	(40)	480 ms		
475	(21)			
430	(28)	430 vvs		
415	(26)			
		380 m sh		378 w
		372 s		370 w
				324 vw
				300 vw
				284 w
				261 s
				252 w
				244 s
				234 w sh
				200 w sh
		188 m sh		184 m
		158 ms		157 m
				148 w sh
		102 mw sh		109 s
		70 w		72 mb



Infrared spectra of 3:chloroparabenzene diazo-oxide

The far infrared spectrum contains instrumental features - see table (DO-III).

23:Dichloro-benzenediazo-oxide:

4000-2000 cm^{-1}:

A weak absorption occurs at 3080 cm^{-1} in this region which is attributed to both (C-H) stretching vibrations. The (C-N) absorption occurs at 2162 cm^{-1} and has a weak shoulder band at 2200 cm^{-1}, in the spectrum of the solid. This is probably a combination absorption or an overtone.

2000-1000 cm^{-1}:

A fairly broad and intense band occurs at 1608 cm^{-1} in the solid. This is shifted to 1617 cm^{-1} in the methylene dichloride solution spectrum and a poorly defined shoulder peak appears at 1603 cm^{-1}. The more intense absorption 1617 cm^{-1} is assigned as a ν(C-O) absorption and the one at 1603 cm^{-1} to a ν(C-C) vibration. Another ν(C-C) mode gives rise to an intense band at 1559 cm^{-1} in the solid state spectrum. In the solution spectrum however, the main absorption is shifted to 1564 cm^{-1} and a very weak absorption appears at 1530 cm^{-1}.

A medium-strong band occurs at 1488 cm^{-1} this too is probably primarily a (C-C) stretching vibration whereas the absorption at 1423 cm^{-1} is quite likely due to a (C-H) bending mode. The remaining two (C-C) stretches are assigned to the bands at 1309 cm^{-1} and 1190 cm^{-1} both are expected to contain a certain amount of (C-H) bending and some (C-Cl) stretching character as well.

The solid state spectrum contains a band at 1262 cm^{-1} which has a well defined shoulder absorption at 1280 cm^{-1}. In the solution spectra, however, the shoulder band degenerates into a very broad and weak absorption while the main band is shifted to 1257 cm^{-1} in the bromoform spectrum. This is assigned to the (C-N) stretching vibration. The shoulder absorption is probably a combination (e.g. 542 + 742 = 1384; 531 + 564 = 1295 cm^{-1}).

The remaining (C-H) bend is assigned to the absorption 1132 cm^{-1} in the solid state spectrum, the intensity of this absorption decreases quite significantly from strong-medium to medium-weak in the solution spectrum. At least one (C-Cl) stretch is expected to occur in this region and this is assigned to the intense band at 1110 cm^{-1}.

<u>1000-400 cm^{-1}</u>:

This region contains the second (C-Cl) mode together with other out-of-plane and in-plane deformation modes. The intense absorption occuring at 936 cm^{-1} in the solid spectrum is attributed to an out-of-plane (C-H) vibration and the band at 869 cm^{-1} is assigned to the low (C-Cl) stretching frequency. A weak absorption is observed at 890 cm^{-1} in the solid state spectrum this could well be due to another out-of-plane (C-H) deformation. The moderately intense band at 764 cm^{-1} is assigned to the ring.breathing mode and the intense one at 742 cm^{-1} to an in-plane ring deformation.

The low and medium intensity bands at 672 and 602 cm^{-1} in the solid state spectrum are probably due to out-of-plane (C-C) vibrations. An absorption occurs at 531 cm^{-1} in the solid spectrum which has a broad shoulder peak at 542 cm^{-1}; in the CH_2Cl_2 solution spectrum, however, the two absorptions become quite distinct and occur at 538 and 530 cm^{-1}; the former is assigned to an in-plane (C-N-N) deformation, and the latter to an out-of-plane (C-N-N) mode. The remaining bands in this region are those at 473, 422 and 416 cm^{-1} in the solid state spectrum; both are relatively weak absorptions. The first and last are nevertheless possibly best assigned to the (C-O) and (C-N-N) in-plane bending modes.

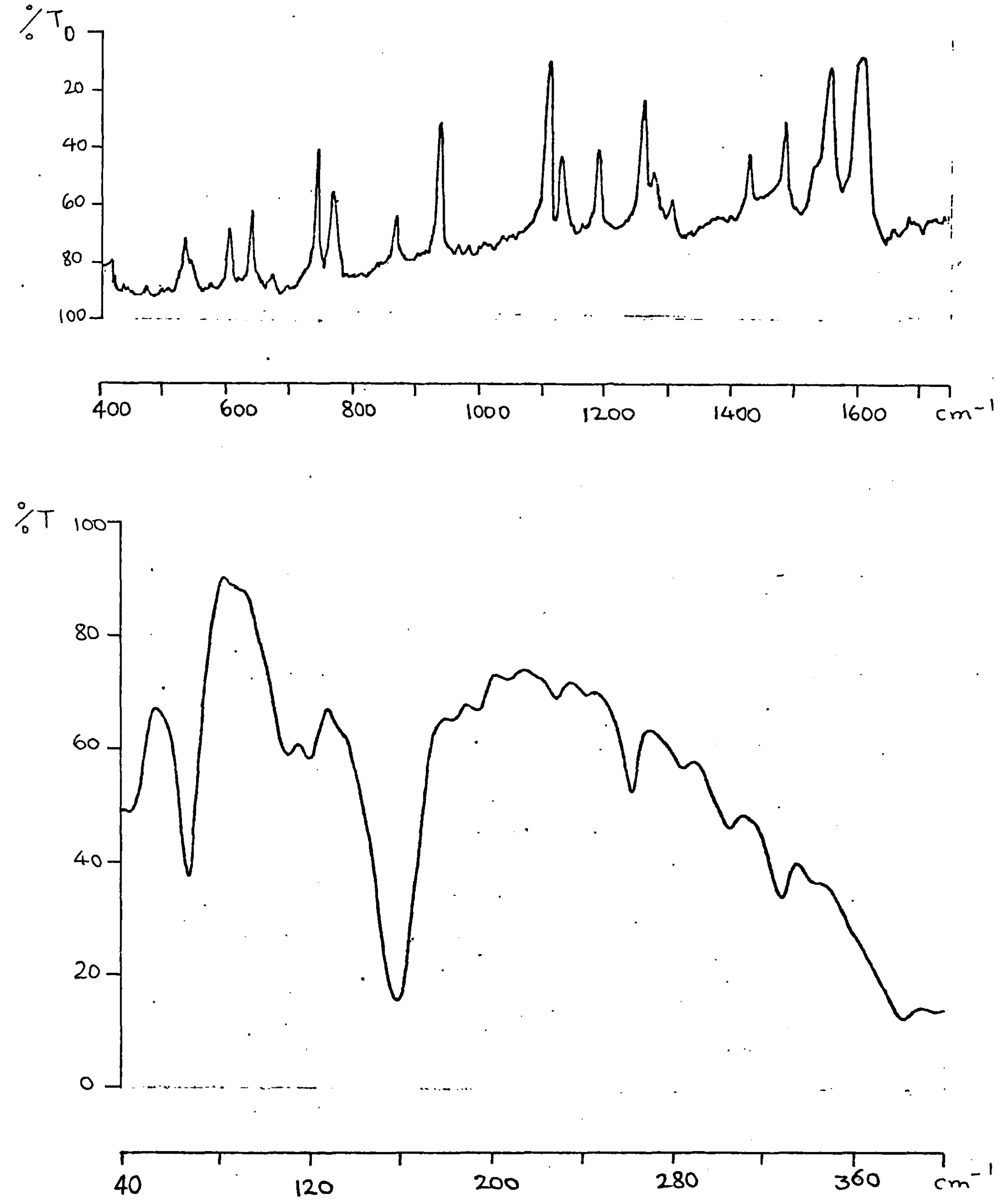
The Raman spectrum of this compound suffers from its fluorescent nature, nevertheless it is possible to derive a certain amount of support for the assignments listed in table (DO-VIII). The Raman shifts observed below 400 cm^{-1} correspond rather closely to some of the far infrared absorptions. A possible set of assignments for the modes normally giving rise to absorptions below 400 cm^{-1} is also given in table (DO-VIII). The two absorptions which have relatively high intensities in the far infrared spectrum are the ones at 276 and 124 cm^{-1}. These are assigned to (C-N-N) and (C-O) out-of-plane vibrations respectively.

Table DO-IV

Observed Spectra of 2,3:Dichloro parabenzene diazo-oxide

NJ	Raman	CH_2Cl_2	$CHBr_3$
* Ī	* Ī	* Ī	* Ī
3080 (7)			
2161 (52)		2182 (52)	2140 (66)
			2120 (35)
		1617 (45)	1613 (60)
1608 (60)	1606 vw	1603 (20) sh	1603 (42) sh
1559 (48)		1564 (36)	1565 (40)
1544 (40) sh		1556 (12) sh	1560 (30) sh
1538 (15) sh		1530 (2) b	
1488 (28)	1485 m	1488 (18)	1490 (20)
1429 (22)	1428 m	1423 (10)	1430 (15)
1309 (11)	1308 m		
1280 (14) sh			1274 (16) sh
1262 (38)			1257 (47)
1190 (26)	1186 vw	1190 (12)	1187 (35)
1132 (20)		1130 (11)	
1110 (50)	1106 vw	1105 (50)	1105 (67)
936 (38)		932 (34)	933 (42)
		890 (7)	
869 (13)	868 m	865 (16)	866 (25)
764 (27)	766 vs		755 (15)
742 (92)			743 (34)
672 (5)			
638 (21)		638 (16)	
602 (18)		599 (12)	
542 (11) sh		538 (8)	
531 (12)		530 (7)	Far Infrared
473 (5) b			
422 (5)			380 w
416 (10) b	414 w		348 w
			276 m
	346 mw		236 w
	260 mw		212 w
			197 w
	205 w (?)		187 w
			176 vw (sh.ur)
			154 vw (sh.ur)
			146 vw (sh.ur)
			124 vs
			84 w (sh.ur)

sh. = shoulder
ur. = unresolved



Infrared spectra of 2,3:dichloroparabenzene diazo-oxide.

The far infrared spectrum contains instrumental features - see table (DO-IV).

2,5:Dichloro parabenzenediazo-oxide:

4000-2000 cm^{-1}:

Three weak absorptions are observed in the (C-H) stretching region. The most intense occur at 3097 and 3051 cm^{-1} and the weakest at 3070 cm^{-1}. The first absorption is probably somewhat higher than expected and could possibly be due to a combination or overtone.

It should, however, be mentioned that possible combination may also be found which would fit the wavenumbers 3070 and 3051 cm^{-1}. The weak absorptions at 2612, 2428, 2364 and 2340 cm^{-1} may be assigned to the combinations and overtones, listed in table (DO-XI). The (C-N-N) stretching absorption is observed at 2118 cm^{-1} in the solid state spectrum and at 2105 cm^{-1} in the solution spectra, the absorption is rather unsymmetric in both phases showing a very obscure shoulder absorption on the high wavenumber side. The position of the antisymmetric ν(C-N-N) absorption is slightly higher in the solid than the corresponding bands in p-benzenediazo-oxide and 2,6:dichlorobenzenediazo-oxide and possibly due to some degree of non-coplanarity with the ring.

2000-1000 cm^{-1}:

The absorption pattern in the region 1550-1620 cm^{-1} consists of two distinct absorptions at 1580 and 1599 cm^{-1} both of which have shoulder bands in the solid state. The main absorptions at these wavenumbers are assigned to ν(C-C) and ν(C-O) modes respectively and the shoulder band at 1614 cm^{-1} to a (C-C) stretching vibration. The medium intensity band at 1439 cm^{-1} in the solid state spectrum is allocated to another (C-O) stretching mode, and the remaining (C-C) vibrations are assigned to the medium absorption at 1349 cm^{-1} and the weak one at 1222 cm^{-1}. The NCA which is based on the force field given in the tables (DOXIII), shows all the (C-C) stretching vibrations to contain considerable amounts of β(C-H), ν(C-Cl) and β(C-N-N) bending motion. The contribution of the latter to (C-C) modes originating from a_1, normal modes of p-benzenediazo-oxide and 2,6:dichloro p-benzenediazo-oxide is less than to the b_2 normal modes but is, nevertheless, significant. This feature is shared by the other non-symmetric diazo-oxides, i.e. 3:chloro and 2,3:dichloro p-benzenediazo-oxide. The intense absorption found at 1260 cm^{-1} in the solid state spectrum is assigned to the second (C-N-N) stretching vibration, it is not observed in the Raman spectrum which possesses only two weak bands at 1580 and 1175 cm^{-1} in the region 1000-2000 cm^{-1}. The Raman spectrum of this compound is not, however, very useful due to some degree of fluorescence and to the instability of the diazo-oxide even in the path of the unfocused laser beam. Two (C-H) in-plane bends and at least one (C-Cl) stretching mode are expected in the range 1000-1400 cm^{-1}. The intense and rather broad absorption at 1170 cm^{-1} is similar to the one observed in the case of 2,6:dichloro p-benzenediazo-oxide. The normal co-ordinate analysis however, shows that a lesser amount of ν(C-N) character is associated with the two frequencies calculated at 1188 and 1148 cm^{-1}, than in the case of the symmetric isomer. Instead they appear to be primarily due to (C-H) bending and (C-Cl) stretching modes. The frequencies calculated at 1046 and 883 cm^{-1} appear to contain a still higher proportion of ν(C-Cl) vibration. The four absorptions observed at 1181, 1170, 1055 and 893 cm^{-1} in the solid state spectrum are therefore provisionally allocated to two β(C-H) and two ν(C-Cl) modes.

1000-40 cm^{-1}:

Four absorptions are observed in the region 1000-800 cm^{-1} one of these is probably due to a ν(C-Cl) mode and the remaining bands are assigned to two (C-H) out-of-plane deformations and a combination vibration as shown in table (DO-X). The bands found at 770 and 680 cm^{-1} in the infrared spectra of the solid give rise to intense lines in the Raman effect, they are assigned to a ring breathing mode and in-plane (C-C-C) deformation. An alternative assignment for these two modes is to the bands at 846 and 770 cm^{-1}. The only other lines observed in the Raman spectrum of this region are the weak ones at 595, 480 and 430 cm^{-1}. The first probably corresponds to the infrared band observed at 587 cm^{-1}, which is assigned to an in-plane (C-N-N) deformation.

The higher out-of-plane mode is assigned to the medium intensity absorption at 420 cm^{-1}. And the β(C-O) mode to the band at 489 cm^{-1}. A set of possible assignments for the remaining modes in this region is given in table (DO-VIII).

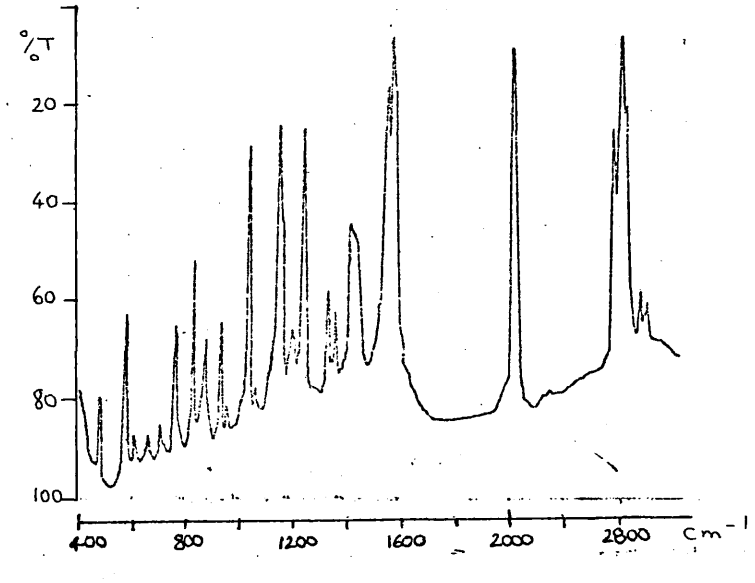
Observed Spectra of 2,5:Dichloro parabenzene diazo-oxide

Table DO V

IR (NJ)	Raman	CH_2Cl_2	$CHBr_3$
* I	* I	* I	* I
3097 (3)			
3070 (1)			
3051 (4)			
2612 (2)			
2428 (1)			
2364 (3)			
2340 (1)			
2118 (16)		2105 (6.2)	2105 (10)
1614 (14) sh		1616 (6)	1612 (9.5)
1599 (16)	1580 w	1582 (6)	1580 (9.3)
1580 (15) sh			
1562 (12) sh			
1542 (7) sh			
1518 (4) sh			
1439 (4)		1428 (3)	1434 (4)
1349 (4)		1455 (3)	1357 (46)
1307 (5)			
1260 (11)			1268 (7.5)
1222 (3)			1256 (4.3) sh
1181 (7.5)	1175 w	1180 (2.2)	1180 (7.4)
1170 (13)			
1147 (0.3)			
1081 (3.5)			
1055 (13)		1050 (2.7)	1052 (7.1)
977 (1)	975 w	960 (0.4)	957 (2.3) sh
955 (5)		948 (0.8)	951 (2.6)
893 (5)		897 (0.8)	
846 (8.5)		873 ([illegible])	873 (5.8)
795 (0.7) b			
776 (5.5)	770 s		778 (3.0)
723 (1.5)			
680 (2.5)	685 s		
671 (2)			
625 (2)		634 (0.2)	
		600 (0.1)	
587 (8)	595 vw	586 (0.7)	539 (4.4)
489 (4)	480 w	482 (0.5)	478 (10)
420 (6)	380 mw		

Table (DO V) cont.

Far Infrared	Raman
380 (w)	
314 (ms)	316 w
278 (m)	268 w
215 (w)	
210 (w) sh	
162 (w)	
146 (w)	
120 (w)	
90 (w) sh?	
85 (w)	



infrared spectrum of 2,5:dichloro p-benzene diazo-oxide

2,6:Dichloro parabenzenediazo-oxide:

4000-2000 cm^{-1}:

The two (C-H) stretching modes in 2,6:dichlorodiazo-oxide are split and show two doublets. The two doublets have centres at 3063 and 3033 cm^{-1}.

An intense shoulder band is associated with the (C-N-N) absorption. The shoulder band occurs at 2151 cm^{-1} in the solid state spectrum but it is shifted to 2076 cm^{-1} in the CH_2Cl_2 and $CHCl_3$ solutions.

Variation of the solute concentration seems to have no effect upon the position or relative intensity of the shoulder band; neither do temperature changes in the range 30-80°C. Addition of a small amount of ethanol to these solutions, shifts the main absorption at 2110 cm^{-1} to a new position at 2135 cm^{-1}, leaving a weak and rather broad band at 2080 cm^{-1}. Ethanol and methanol solutions exhibit the same effect. It must be concluded therefore that the shoulder absorption is probably an overtone or a combination tone which borrows intensity from the main ν(C-N-N) absorption. Table (DO-VII).

2000-40 cm^{-1}:

The ν(C=O) and ν(C=C) a_1 stretching modes are assigned to the intense and broad infrared absorption at 1617 cm^{-1} in the methylene chloride solution spectrum. This absorption probably corresponds to the medium-strong intensity Raman lines at 1610 and 1594 cm^{-1}.

The high intensity Raman line at 1563 cm^{-1} is assigned to another (C-C) stretching vibration which gives rise to infrared absorption at

1573 cm^{-1} in the solid. This is a sharp and intense absorption in the solution spectrum but becomes rather broad and has associated shoulder absorptions in the solid. It is predicted by the NCA to contain a certain amount of (C-N-N) bending character.

The remaining (C-C) stretching absorptions are expected to occur in the region 1500-1100 cm^{-1}. The medium intensity band occuring in the Raman and infrared spectra at 1442 and 1443 cm^{-1} respectively assigned to another, b_2, (C-C) stretching vibration. The remaining, a_1 and b_2 ν(C-C) modes are allocated to the bands at 1355 and 1306 cm^{-1} in the solid and solution spectra respectively. The former absorption is more intense and appears to contain a substantial amount of (C-N) stretching character, while the latter seems to be associated with some (C-H) bending motion and has a higher intensity in the Raman spectrum.

The (C-N) stretching vibration is assigned to the intense and rather broad band at 1178 cm^{-1} in the solid state spectrum. This appears to become split and moves down to about 1160 cm^{-1} in the spectrum of the solution. Two shoulder absorptions are connected with this band in both phases. The one at 1190 cm^{-1} in the solid state spectrum is assigned to a β(C-H) mode and the one at 1152 cm^{-1} to a ν(C-Cl) / β(C-H) vibration. The Raman spectrum in this region also contains two lines, a very strong one at 1164 cm^{-1} and a rather intense one at 1152 cm^{-1}. The only band left above 1000 cm^{-1} is the one at 1056 cm^{-1} in the solution spectrum, this is assigned to another β(C-H)/ν(C-Cl) mode. The remaining ν(C-Cl) vibration is allocated to the relatively strong absorption at 876 cm^{-1} in the solid state spectrum. The NCA predicts a predominantly ν(C-Cl) b_2 mode at 895 cm^{-1}. It also shows that a certain amount of mixing with β(C-C-N) motion might also be expected.

The out-of-plane γ(C-H) vibrations are assigned to the infrared absorptions at 964 and 908 cm^{-1}. The corresponding Raman lines are probably the strong shifts at 960 and 906 cm^{-1}. In the solid state infrared spectrum the lower absorption is split into three bands at 919, 908 and 903 cm^{-1}. This may possibly be due to the structure of the unit cell. A similar situation occurs in the case of the solution absorption at 512 cm^{-1} which is also split into three distinct absorptions occuring at 527, 521 and 512 cm^{-1}. The Raman spectrum contains a single line in both cases. The possibility of some of these absorptions being due to overtone or combination tones has been investigated and probable combinations are listed in table (DO-XI).

The ring breathing mode and the two, a_1; α(C-C-C) modes are allocated to the absorptions at 794 and 779 and 372 cm^{-1}. The latter two absorptions are shown to possess some in-plane (C-Cl) bending character. The b_2; α(C-C-C) mode is assigned to the absorption at 639 cm^{-1}, which probably contains a large degree of β(C-O) and β(C-N-N) character.

The preferred assignments of the vibrational modes in the remaining region are shown in table (DO-VIII).

Observed Spectra of 2,6:Dichloro p-Benzenediazo-oxide

Table DO-V I

NJ			Raman		CH_2Cl_2			$(CD_3)_2CO$	
*	I		*	I	*	I		*	I
								3083	(55)
								3062	(30)
								3050	(45)
								3030	(30)
2152	(5.6)	sh							
2110	(8.0)								
1620	(5.0)		1610	m	1617	(6.0)			
1573	(5.8)		1580	(b)	1570	(7.0)			
[illegible]			1563	m					
1527	(0.5)				1526	(1.1)			
			1443	mw					
1355	(1.5)				1356	(1.5)			
			1306	ws					
1190	(3.3)	sh	1164	vs					
1178	(4.7)		1152	s					
1056	(0.7)		1065	m					
1041	(0.2)		1044	m					
1020	(0.3)	b	1002	mw					
964	(3.5)		960	s					
958	(4.0)								
950	(3.0)				937	(0.2)			
919	(3.5)								
908	(4.5)		906	s					
903	(4.0)				903	(2.7)			
					897	(1.0)	sh		
					893	(1.3)			
876	(3.8)		836	vvw	871	(1.8)			
			830	vvw					
806	(3.6)				800	(3.0)			
794	(5.8)		795	vvw	794	(1.7)			
779	(3.7)		780	w					
763	(6.2)								
675	(0.2)		672	vvw	669	(0.5)			
					668	(0.3)			
644	(2.2)		660	vvw					
639	(0.9)		650	vvw					
527	(1.7)		528	w					
521	(2.2)								
512	(2.4)								
482	(2.3)								
466	(0.8)								
424	(0.5)		470	w					

Table(DOVI) Cont.

Far Infrared	Raman
382 (mw)	388 (m) sh
365 (s)	372 (ms)
330 (vvw)	308 (m)
287 (m)	
219 (vw)	204 (vw)
190 (vw)	
168 (w) b	161 s
140 (w)	136 (mw) sh
105 (m) b	110 (w) sh
85 (m)	80 (m) sh

The infrared spectrum of 2:Chloroparabenzenediazo-oxide was recordedin the region 650-5000 cm^{-1} using a Nujol mull of the compound, and a tentative assignment of the absorptions observed in this region is attempted.

Region 5000-2000 cm^{-1}:

The (C-H) stretching absorptions are observed as a relatively weak band at 3070 cm^{-1}, with unresolved shoulder absorptions at 3050 and 3090 cm^{-1}. The (C-N-N) stretching absorption occurs at 2115 cm^{-1} and constitutes the most intense band in this region.

Region 2000-1000 cm^{-1}:

The ν(C-O) and ν(C-C) modes which occur in this region are assigned in accordance with the pattern found for the other diazo-oxide. The ν(C-O)/ ν(C-C) absorptions give rise to a characteristically broad and intense absorption having a maximum at 1570 cm^{-1}.

The second ν(C-N-N) vibration may also be assigned in analogy with the other diazo-oxides: to the medium intensity absorption at 1232 cm^{-1}. This absorption has two shoulder bands at 1239 and 1221 cm^{-1}which may be assigned to a ν(C-C) and β(C-H) vibration.

The (C-Cl) stretching vibration is expected to give rise to a somewhat intense absorption in the region 1100-1000 cm^{-1}. The only strong absorption observed in this region occurs at 1114 cm^{-1} and is split into a doublet, a somewhat weaker absorption occurs at 1018 cm^{-1}. The reverse of this situation was observed in the case of 3:chloro parabenzenediazo-oxide, which has an intence band at 1018 cm^{-1} and a much weaker one at 1105 cm^{-1}, which were assigned to ν(C-Cl) and β(C-H) modes respectively. Asimilar assignment may be made in the case of the 2:chloro derivative.

Two bands remain to be assigned in this region, both are quite intense and occur at 1147 and 1135 cm^{-1}, the first is perhaps best allocated to the lowest (C-C) stretching vibration in conformity with the previous assignments for the other diazo-oxides and the second, less intense absorption, to the third β(C-H).

Region 1000-650 cm^{-1}:

The γ(C-H) modes are assigned to the bands at 903, 878 and 818 cm^{-1}. This leaves the absorption at 830 cm^{-1} to be assigned to the ring breathing mode and the two bands at 772 and 760 cm^{-1} to in-plane and out-of-plane (C-C) deformations. The medium intensity band observed at 660 cm^{-1} may be allocated to an in-plane (C-C) bend.

Assignment of some Fundamental Vibrations of 2:Chloro p-benzenediazo-oxide

Table (DO-VIA)

ν(C-H)	3075	ν(C-C)	1239	RB	830
ν(C-H)	3050	ν(C-C)	1147	α(C-C-C)	772,760
ν(C-N-N)	2115	β(C-H)	1360	α(C-C-C)	660
ν(C-O)	1575	β(C-H)	1135	α(C-C-C)	–
ν(C-C)	1580	β(C-H)	1114	γ(C-H)	903
ν(C-C)	1540	ν(C-N-N)	1232	γ(C-H)	878
ν(C-C)	1472	ν(C-Cl)	1018	γ(C-H)	818

Table (DO - VII)

Summary of Solution Studies on 2,6:Dichloro p-Benzenediazo-oxide

Solvent	Band I	Band II	Relative Intensity(1)	Concentration(2)
CH_3OH	2138			20.53
C_2H_5OH	2134	2080	60	33.36
	2135	2080	63	25.22
	2135	2084	60	20.19
	2135	2080 b	60	16.17
	2135	2080 b*		12.04
CH_2Cl_2	2109	2070	50	4.05
$CHCl_3$	2105	2076	55	4.26
	2105	2076	55	2.97
	2105	2076	56	2.13
C_6H_6	2104	2080	66	(3)

*The relative intensity of band II is less than 0.2% which is approximately the estimated error due to base line instability.

(1) Intensity (I)/Intensity (II) X 100.

(2) Gramme Molecule per gramme of solvent X 10^{-6}

(3) Saturated solution.

Table DO-VIII

Assignments of Fundamentals in the Spectra of the Diazo-oxides

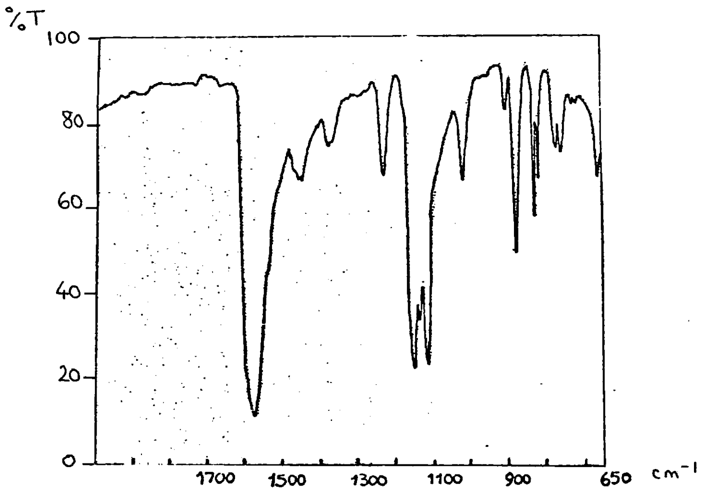
	DO	3DO	23DO	25DO	26DO
ν CH	3070	3075	3080	3070	3083
ν CH	3040			3051	3050
ν CNN	2100	2116	2182	2118	2110
ν CO	1587	1600	1617	1599	1620
ν CC	1612	1625	1603	1614	1620
ν CC	1605	1550	1558	1580	1573
ν CC	1398	1450	1488	1439	1443
ν CC	1315	1270	1309	1349	1355
ν CC	1220	1195	1190	1222	1306
β CH	1387	1380	1429	1181	1190
β CH	1145	1121	1132	1170	1152
β CH	1110	1105	1132	1170	1152
β CH	1095				
ν CNN	1245	1234	1262	1260	1174
ν CCl		1019	1110	1055	1065
ν CCl			869	893	876
RB	775	854	764	846	794
α CCC	720	726	742	776	779
α CCC	690	693	638	680	512, 639
α CCC	446	380	380	380	372
β CNN	502	475	538	587	527
β CNN		415	416	314	387, 466
β CO	415	430	473	489	424
β CCl		158	212, 236	210	204
β CCl			187	162	161
γ CH	978	967	936	977, 846	964
γ CH	950	869	890	955, 846	908
γ CH	844	803			
γ CH	810				
ϕ CC	770	680	672	723	763
ϕ CC	630?	598	602	625	644
ϕ CC	462	372	422	(268)	372
γ CNN	450	487	542 538	420	482
γ CNN		184, 284	276	215, 314	136, 387
γ CO		102, 158	146	146	161, 136
γ CCl		70, 102	124	120	110
			84	85	80

Table (DO- IX)

Observed Spectrum of 2:Chloroparabenzene-diazo-oxide (Nujol mull).

3090 (3) sh
3070 (5)
3050 (3)
2115 (81)
1580 (75)sh
1570 (80)
1540 (69)sh
1472 (12)
1360 (14)sh
1239 (15)sh
1232 (23)
1221 (14)sh
1147 (68)
1135 (54)sh
1117 (66) d
1110 (66)
1080 (10) b
1018 (24)
905 (10)
880 (21)
878 (41)
830 (28)

818 (27)
772 (19)
760 (20)
722 (2) d
719 (2)
660 (14)



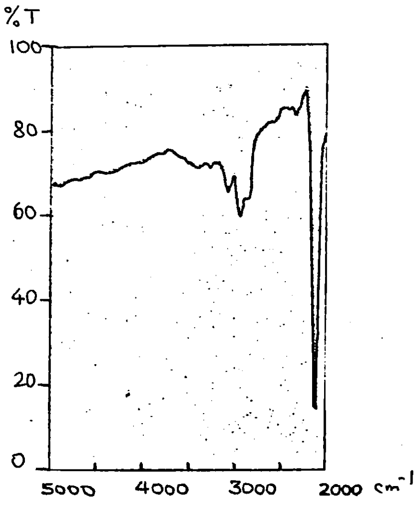


Table DO- X

(X-N-N) Stretching Frequencies

XNY	HN_3[50]	CH_3N_3[51]	CH_3NCO[51]	Diazomethane[53]	$C_6H_4ON_2$	$3:Cl.C_6H_3ON_2$	$2,3:Cl_2C_6H_2ON_2$
as	2140	2143	2232	2101	2100	2116	2182
s	1269	1295	1412	852	1245	1234	1262
mean	1704	1719	1822	1476	1672	1675	1722
def_1	739	790	652	586, 487	450	487	542, 538
def_2	658	654	607	487, 456	-	284, 184	276

Possible Combination Bands of the Benzene Diazo-oxides

Parabenzene diazo-oxide in cm^{-1}

Table (DO- XI)

3010	1398 + 1612	= 3010	0
	1398 + 1605	= 3003	7
	1587 + 1398	= 2981	29
	2100 + 502 + 415	= 3017	7
	2100 + 1462 + 450	= 3012	2
1455	775 + 690	= 1465	10
	950 + 502	= 1452	3
707			
630			
3:Chloro parabenzene diazo-oxide			
676	372 + 284	= 656	20
567	380 + 188	= 568	1
2,3:Dichloroparabenzenediazo-oxide			
1280	672 + 602	= 1274	6
	869 + 416	= 1285	5
	890 + 380	= 1270	10
	742 + 552	= 1273	7
2,5:Dichloroparabenzene diazo-oxide			
2612	1574 + 1055	= 2629	17
	1439 + 1181	= 2620	8
2428	2118 + 314	= 2430	4
	1260 + 1170	= 2430	2
2364	2118 + 268	= 2386	22
	1594 + 766	= 2360	4
2340	1614 + 723	= 2337	3
	1580 + 770	= 2350	10
	1439 + 893	= 2335	5

Table (DO- XI)(Cont.)

2,6:Dichloro parabenzene diazo-oxide

2151	1620 + 527 = 2147	4
	1355 + 794 = 2149	2
	1190 + 964 = 2154	3
1443		
	1355 + 80 = 1435	8
	1306 + 136 = 1442	1
	1065 + 372 = 1437	6
	1065 + 388 = 1453	10
	794 + 639 = 1433	10
	794 + 644 = 1438	5
	964 + 482 = 1446	3
	908 + 527 = 1435	8
1306		
	1443 - 136 = 1307	1
	1190 + 110 = 1300	6
	1152 + 160 = 1313	7
	1174 + 136 = 1310	4
	876 + 424 = 1300	6
	794 + 512 = 1306	0
	779 + 527 = 1306	0
	388 + 908 = 1296	10
950		
	1152 - 204 = 948	2
	1065 - 110 = 955	5
	876 + 80 = 956	6
	794 + 161 = 955	5
	779 + 161 = 940	10
	466 + 482 = 948	2
	424 + 527 = 951	

Table (DO- XI)(Cont.)

Observed	Possible Combinations	Difference
919	2110 - 1190 = 920	1
	1306 - 388 = 918	1
	779 - 136 = 915	4
	527 + 388 = 915	4
	763 + 161 = 924	5
903	1065 - 161 = 904	1
	794 + 110 = 904	1
	512 + 388 = 900	3
	527 + 372 = 899	4
	482 + 424 = 906	3
	763 + 136 = 899	4
806	2110 - 1306 = 804	2
	1443 - 693 = 804	4
	639 + 161 = 800	6
	424 + 388 = 812	6
	424 + 372 = 796	10
675	1190 - 512 = 678	3
	1065 - 388 = 677	2
	875 - 204 = 672	3
	512 + 161 = 673	2
	466 + 204 = 670	5
639	1152 - 527 = 640	1
	1065 - 161 = 641	2
	512 + 136 = 648	9
	482 + 161 = 643	4
	527 + 110 = 637	2
527	1306 - 779 = 527	0

Observed	Possible Combinations	Difference
1020	1443 - 424 = 1019	1
	876 + 136 = 1012	8
	512 x 2 = 1024	4
	639 + 372 = 1011	9
	639 + 388 = 1027	7
	908 + 110 = 1018	2
958	2110 - 1152 = 958	0
	876 - 80 = 956	2
	794 + 161 = 955	3
	527 + 424 = 951	10
	763 + 204 = 967	9
	482 x 2 = 964	6

Normal Co-ordinate Treatment of the Diazo-oxides

The calculated planar frequencies of some p-benzenediazo-oxides are listed in table (DO- XII-A). The initial force fields used in these calculations are developed for parabenzoquinone in this work and Annos set (A-II), table (Q- XI). These force field parameters were "improved" using sets of experimental frequencies taken from slightly different assignments developed earlier on the basis of solid and solution infrared measurements in a narrower spectral region.

The only two diazo-oxides considered here which have any symmetry at all are the parent compounds and the symmetrically substituted dichloro derivative. The "improved" force constants derived from these compounds are tested with the other diazo-oxides and the process repeated if agreement is not satisfactory. The force constants of table (DO- XII-B) suffer from the same disadvantages mentioned in the case of the quinone force constants, there being some uncertainty regarding the parameters involving (C-C) stretching and (C-H) bending motion.

The force field used in the calculations summarised in table (DO- XII), ignores differences between parameters involving β(C-O), β(C-N) and β(C-H) interactions with other co-ordinates. The force field given in table (DO-XIII), however, takes into account such differences for the parent compound and its chloro derivatives.

Some of the parameters were refined using the final assignments for these compounds. The agreement between the observed and calculated results is not as good as it was with the refined force field of table (DO-XIIB). The more detailed description of the potential energy of these systems, which is implied by the final force field must nevertheless constitute an initial improvement on the former.

The non-planar vibrations of the diazo-oxides were calculated using as a first approximation the force field parameters given as set (I) in table (DO-XV-A). The diagonal force constants involving γ(C-N-N) deformations were assumed to be approximately equal to the corresponding γ(C-O) parameters of p-benzoquinone and the non-diagonal constants were ignored. The remaining parameters are based upon the p-benzoquinone parameters of table (Q- XXII) set III. The resulting frequencies are given in table (DO- XV-A). The potential energy distribution and Cartesian displacement figures obtained with the frequencies show that the γ(N-N) character is not entirely localised. To take 2,6:dichloro p-benzene diazo-oxide as an example it may be seen from table (DO- XVI) that substantial γ(N-N) motion is involved in the modes numbered 3, 4, 5, 7 and 9. Only the first four however, are of γ(N-N) type.

Table (DO-XVII) contains sets of non-planar vibrational frequencies for parabenzene diazo-oxide calculated using different values for the γ(N-N) force constant. The results of this calculation illustrate the dependence of the calculated frequencies and their potential energy contributions upon this diagonal force constant. It is immediately apparent from inspection of the potential energy figures that while the γ(N-N) character is shared out among a number of frequencies only two of the calculated frequencies are more sensitive than the rest to changes in the value of γ(N-N). They are the ones labelled 4 and 6 in Table (DO-XVII). A value of about 0.5×10^{-11} erg. rad^{-2} for the diagonal (N-N) bending vibration appears to be consistent with the assignments produced for the diazo-oxides in this work and those found for other similar molecules Table (DO-VIII). It should however be remembered that non-diagonal constants involved in the γ(C-N-N) vibration were assumed to be equal to zero in the above mentioned calculation.

In addition to this there is the effect of other parameters not directly involved in (C-N-N) bending but which nevertheless make a non-zero potential energy contribution towards the γ(C-N-N) frequencies.

The calculations of the non-planar vibrational frequencies of parabenzene diazo-oxide has therefore been carried out using the force field parameters found for parabenzoquinone as the result of a refinement process which uses the well established assignments of parabenzoquinone-h_4 and parabenzoquinone-d_4 Table (DO-XVA) Set (II) the results, which are summarised in Tables (DO-XVIII), appear to point in the same direction as those of table (DO- XVII).

An experiment aimed at studying the effect of the non-diagonal force constants concerned with the (N-N) vibration shows that the frequencies and potential energy distributions are not altered very significantly when the force constants are changed within reasonable limits. Table (DO- XIX) shows the influence of changing the force constant f $\left[\gamma(\text{N-N})/\ \gamma(\text{C-N})\right]$, which is the most important of the γ(N-N) non-diagonal constants.

Calculated Planar Vibrations of some Diazo-oxides

Table (DO- XIIA)

	DO		25DO		26DO	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	3072	3083	3070	3078	3066	3070
2	3069	3074	3049	3054	3061	3064
3	3068	3064	2118	2121	2110	2107
4	3050	3047	1626	1670	1620	1637
5	2105	2106	1615	1624	1620	1627
6	1612	1619	1580	1608	1574	1560
7	1605	1606	1550	1508	1527	1549
8	1590	1583	1353	1350	1354	1380
9	1481	1485	1255	1304	1278	1284
10	1479	1475	1225	1210	1180	1252
11	1315	1312	1180	1178	1178	1162
12	1265	1287	1170	1106	1155	1105
13	1216	1202	1051	1043	1058	1024
14	1145	1128	895	887	875	884
15	1096	1059	776	812	794	829
16	978	976	670	691	772	755
17	845	874	587	587	512	517
18	728	714	489	484	466	437
19	690	679	430	425	427	425
20	677	648	290	310	395	355
21	500	491	250*	257	250*	251
22	415	410	180*	182	180*	175
23	270*	260	160*	164	160*	168

*Assumed.

Planar Force Field Parameters Used for the Benzene diazo-oxides

Table (DO-XIIB)

No.	Description	DO	25DO	26DO
1	101	2.3000	2.3683	2.3683
2	102	0.4554	0.4109	0.3974
3	108	-0.1878	-0.1166	-0.1946
4	213	-0.2515	-0.2515	-0.2861
5	119	-0.5003	-0.2567	-0.3166
6	707	2.4087	1.8611	1.8611
7	808	0.9960	1.0171	1.0171
8	708	0.0193	-0.0581	-0.0581
9	709	-0.0153	-0.0506	-0.0503
10	710	-0.0179	-0.0135	-0.0135
11	713	-0.0545	-0.1085	-0.1085
12	714	0.0534	0.0388	0.0388
13	819	-0.4832	-0.2420	-0.2420
14	1222	-0.0600	0.2382	-0.2213
15	1313	4.6000	4.1729	4.2029
16	1414	7.3000	6.5709	6.5709
17	1415	0.8352	0.8395	0.8395
18	1315	-0.9754	-0.9815	0.3116
19	1316	-0.0300	-0.0389	-0.0389
20	1416	-0.0688	-0.3329	-0.1436
21	1318	0.6526	0.1417	0.1417
22	1319	1.2197	0.6140	0.6140
23	1322	0.3154	0.2619	0.2619
24	1417	0.0280	0.0280	0.8598
25	1419	-0.2187	-0.1786	-0.1786
26	1919	9.0000	8.9522	8.9522
27	2222	5.7000	5.2502	5.2502
28	2020	5.0930	5.0930	5.0930
29	2021	0.0250	0.0250	0.0250
30	2024	-0.0400	-0.0400	-0.0400
31	2023	0.0080	0.0080	0.0080
32	2525	17.3000	17.6550	17.6750
33	1425	0.0000	0.0000	0.0000
34	1625	0.0000	0.0000	0.0000
35	1825	0.0000	0.0000	0.0000
36	2225	0.8000	0.8000	0.8000
37	425	0.0000	0.0000	0.0000
38	825	0.0000	0.0000	0.0000
39	925	0.0000	0.0000	0.0000
40	2626	1.3600	2.4710	2.4710
41	426	0.2740	0.0500	0.0000
42	626	0.0000	0.0000	0.0000
43	326	0.0000	0.0000	0.0000

Table (DOXIIC)

Force Field Parameters Involving (C-Cl) Vibrations

Description	25DO	26DO
808	1.2000	1.2000
819	-0.2382	-0.2213
1920	0.6040	0.4483
1923	0.1749	0.0000
920	0.1665	0.1696
1220	0.0366	0.0366
1320	0.4483	0.6525
2020	4.3946	4.3904

Table (DO XIII)

Planar Force Field Parameters for the Diazo-oxides

Description	DO	3DO	23DO	25DO	26DO
101	2.3000	2.3600	2.3683	2.3683	2.3683
202	2.3000	2.3600	2.3683	2.3683	2.3683
303	2.3000	2.3600	2.3683	2.3683	2.3683
102	0.4553	0.4000	0.4109	0.4109	0.39745
108	-0.1877	-0.1700	-0.1106	-0.1106	-0.1106
119	-0.5003	-0.1339	-0.1339	-0.5003	-0.3519
113	-0.2515	-0.1756	-0.1756	-0.1756	-0.2798
214	-0.2515	-0.1756	-0.1756	-0.1756	-0.2798
707	2.4106	1.8700	1.8700	1.8611	1.8611
1010	2.4106	1.8700	1.8700	1.8611	1.8611
710	-0.0179	-0.0134	-0.0134	0.0000	0.0000
708	0.0193	-0.0581	-0.0581	-0.0581	-0.0508
709	-0.0153	-0.0503	-0.0153	-0.0153	-0.0203
713	-0.0545	0.0000	0.0000	-0.1085	-0.1085
714	0.0534	0.0000	0.0000	0.0388	0.0388
808	1.0171	1.0171	1.0171	1.0455	0.9217
809	0.0193	-0.0581	0.0193	-0.0943	-0.0503
812	-0.0425	-0.0583			
811	-0.0248	-0.0134			
819	-0.5000	-0.2400	0.2420	0.2420	-0.2554
822	-0.0600		-0.2382	-0.2382	
813	0.2024	-0.1085	0.2720	-0.1085	
815	0.0545	-0.0400	0.0000	-0.0388	
1313	4.6372	4.6000	5.000	5.0000	
1414	4.6372	7.3000	7.3000	7.3000	
1314	7.8570	0.8400	0.8394	0.8394	
1318	0.8325	0.1400	0.1417	0.1417	
1315	0.6760	-0.7000	-0.9814		0.3116
1416	-0.9700	-0.1400	-0.3329		-0.1437
1316	-0.0688	-0.0400	-0.0389		0.0000
1417	-0.0696	0.8000	0.0280		0.8598
1319	0.0280	0.6140	0.6140		
1422	0.8900	-0.1780	-0.1786		
1322	-0.2180	0.2619	0.2619		

Table (DO XIII) (Cont.)

	DO		3DO		23DO		25DO	26DO
1919	9.0000		8.9900		8.9522		8.9522	8.9522
2222	4.8550		5.2500		5.2500		4.6877	5.2500
1922	0.0000		0.0000		0.0000		0.0000	0.0000
2020	5.0930		5.0930	2323	5.0930		5.0930	5.0930
2021	0.0250		0.0250	2324	0.0250			
2024	0.0400		0.0400					-0.0400
2023	0.0080		0.0080			2124	0.0080	
2525	17.5650		17.7708	1525	18.5903		17.6650	17.6650
2225	0.8049		0.8000		0.8050		0.8049	0.8000
1525	0.0000		0.0000		0.0000		0.0000	0.0000
1425	0.0000		0.0000		0.0000		0.0000	0.0000
2026	1.0246		2.4700		2.4700		1.5825	2.4710
926	0.0000	1126	0.0000	1126	0.0000		0.0000	0.0000
826	0.0000		0.0000		0.0000		0.0000	0.0000
426	0.0000		0.0000		0.0000		0.0000	0.0000
1026	0.0000		0.0000		0.0000		0.0000	0.0000
126	0.0000		0.0000		0.0000		0.0000	0.0000

Table (DO- XIII) Cont.

Force Constants Involving (C-Cl) Vibrations in the Diazo-oxide Force Field

Description	3DO	23DO	25DO	26DO
220	0.0000	0.0000	0.0000	0.0000
120	0.0000	0.0000	0.0000	0.0000
320	0.0000	0.0000	0.0000	0.0000
420	0.0000	0.0000	0.0000	0.0000
808	1.2000	1.2000	1.2000	1.2000
809		0.0000		
812				-0.0503
811			-0.0135	
920	0.2700	0.2720	0.2770	0.1678
923	0.0400	0.0366	0.0366	0.0366
1920	0.6040	0.6040	0.6040	0.4483
1923	0.1645	0.1749	0.1740	0.0000
2020	3.9000	3.9000	3.9000	3.9000
2021		0.0000		
2024				0.0000
2023			0.0000	

Table DO XIV

Calculated Planar Frequencies of some Diazo-oxides

	DO	3DO	23DO	25DO	26DO
1	3085 1	3079 1	3072 1	3069 1	3078 1
2	3077 1	3069 1	3061 1	3064 1	3056 1
3	3065 1	3052 1	2141 2	2099 2	2111 2
4	3046 1	2116 2	1636 3	1627 4,3	1645 3,4
5	2097 2	1673 3,2,4	1590 4,3	1597 3	1622 4,3
6	1655 3,6,9	1648 4,2,3	1533 3,6	1571 3,6	1587 3,9
7	1622 4,3	1546 4,2,3,6	1488 3,6	1539 3,6	1521 3
8	1626 3	1500 3,6,4	1452 6,3	1367 6,3,9,8	1389 3,2
9	1547 4,3,2	1359 3,6	1319 3,6,5,9	1251 3,9	1346 3
10	1458 6,3,4	1327 3,6,8,9	1228 2, 6	1231 2,3,5	1197 2,6
11	1332 6	1250 2,6	1104 2,6,5	1188 6	1195 6,7
12	1258 2,6	1225 6,7,9,5	1156 6	1148 5,6,2	1136 6,5
13	1257 6,9,3	1129 5,9	1011 3,5,6	1046 5	1053 5,9
14	1135 6	1071 6,7	926 5,7	883 5,9	895 5,9,7
15	1071 6,7	988 6,9	896 5,9,7	769 7,3	860 5,3
16	986 2,6	877 5,7	715 9,7	723 9,7	772 7,3
17	878 7,9,8	750 3,7	542 8,9	554 8,7	536 8,7
18	733 3,7	680 7	453 8,9,7	474 8,9,7	445 7
19	655 7	506 7,8	421 7,5	428 7,9	433 9,7
20	649 9,7	443 7	374 7	296 7	370 7
21	507 6,9,7	382 8,9,7	268 8,9,10	269 8,9	269 8,9
22	410 7	262 8,9	169 10	176 10	173 10
23	265 8,9	160 10	146 10	159 10	161 10

1: ν(C-H); 2: ν(C-N-N); 3: ν(C-C); 4: ν(C-O); 5: ν(C-Cl); 6: β(C-H); 7: α(C-C-C)
8: β(C-O); 9: β(C-N-N); 10: β(C-Cl).

Table (DO- XVA)

Non-Planar Force Constants Used in the Diazo-oxide Calculations

		Set (I)	Set (II)			Set (I)	Set (II)
1	101	0.2352	0.1841	16	812	-0.0480	-0.0225
2	202	0.2352	0.2763	17	811	0.0143	-0.0020
3	102	-0.0639	-0.0616	18	108	-0.1537	-0.1743
4	304	-0.0639	-0.0484	19	209	-0.1537	-0.1576
5	105	0.0000	0.0009	20	310	-0.1728	-0.1048
6	103	0.0000	0.0052	21	109	0.0278	0.0542
7	104	0.0000	-0.0062	22	608	0.0291	0.0528
8	205	-0.1426	-0.0945	23	210	0.0541	0.0030
9	707	0.6288	0.5077	24	211	0.0000	-0.0024
10	1010	0.5091	0.4707	25	312	0.0000	-0.0046
11	808	0.4419	0.4372	26	110	0.0000	0.0000
12	708	-0.1065	-0.1448	27	1013	0.0000	0.0000
13	709	0.0039	0.0176	28	1313	0.4000	0.4000
14	710	-0.0193	0.0407	29	313	0.0000	0.0000
15	809	-0.0700	-0.1002	30	213	0.0000	0.0000

Non-Planar Vibrational Frequencies of some Diazo-oxides

Table (DO- XVB)

DO		2DO		3DO		25DO		23DO		26DO
1006	1,2*	923	1,2	942	1,2	942	1,2	929	1,2	927
943	1,2	890	1,2	880	1,2	863	1,2	856	1,2	871
892	1,2	811	1,2	829	1,2	706	2,1,4	691	2,1,4	673
808	1,2	703	2,1,4	667	2,1,4	651	3,2	622	3,2	638
750	2,1,4	628	3,2	639	3,2	474	4,2	459	4,2	438
572	3,2	446	2,4	381	2,4	388	2,4	412	2,4	374
462	2,4	355	2,3	326	2,3	289	2	277	2	298
278	2,3	280	4,3	257	4,3	227	4,3	202	4,3	158
252	4,3	154	2,4,3	157	2,4,3	126	5,2	117	5,2	122
118	2,4,3	115	5,2	80	5	82	5	82	5	105

*These figures indicate contribution from the co-ordinates denoted:

1: γ(C-H); 2:ring deformation; 3: γ(C-O); 4: γ(C-N-N); 5: γ(C-Cl).

Table (DO- XVI)

Cartesian Displacement Figures for 2,6:Dichloro Para-Benzenediazo-oxide

Mode \ Atom	1	2	3	4	5	6	7	8	9	10	11	12	13
1	0.005	0.057	-0.182	0.181	-0.182	0.057	-0.003	-0.000	0.593	-0.036	0.593	-0.000	0.010
2	0.000	-0.059	0.150	0.000	-0.150	0.059	0.000	0.001	-0.645	0.000	0.645	-0.001	0.000
3	-0.091	0.075	-0.084	0.209	-0.084	0.075	0.009	-0.001	-0.238	-0.084	-0.238	-0.001	0.026
4	-0.258	0.189	-0.079	-0.021	-0.079	0.189	0.030	-0.005	0.087	0.043	0.087	-0.005	-0.015
5	-0.045	-0.054	0.104	-0.067	0.104	-0.054	0.027	0.002	0.044	-0.066	0.044	0.002	0.029
6	0.000	0.168	-0.102	0.000	0.102	-0.168	0.000	-0.009	-0.053	0.000	0.053	0.009	0.000
7	-0.010	0.067	0.004	-0.045	0.004	0.067	-0.023	-0.006	-0.050	-0.005	-0.005	-0.006	0.034
8	-0.000	-0.018	0.065	0.000	-0.065	0.018	0.000	-0.007	0.011	0.000	-0.011	0.007	0.000
9	0.005	0.015	0.017	0.004	0.017	0.015	-0.006	-0.007	-0.025	0.003	-0.025	-0.007	-0.019
10	-0.041	0.021	0.004	-0.011	0.004	0.021	-0.017	0.005	0.008	-0.002	0.008	0.005	-0.006

Table (DO -XVII)

The Variation of Frequencies and Potential Energy Figures for p-Benzenediazo-oxide with the γ(N-N) Force Constants. The calculation uses the force field parameters given in table (DO - XVA), set I.

γ(N-N)	0.600		0.500		0.300		0.250	
Number								
1	985	0.009	984	0.007	983	0.005	983	0.004
2	898	0.039	894	0.032	883	0.021	887	0.019
3	733	0.121	723	0.095	710	0.051	708	0.045
4	616	0.231	595	0.281	553	0.291	544	0.267
5	471	0.058	467	0.086	451	0.199	445	0.237
6	304	0.159	294	0.229	271	0.559	261	0.726
7	123	0.048	122	0.070	118	0.205	117	0.299
8	950	0.000	950	0.000	950	0.000	950	0.000
9	807	0.000	807	0.000	807	0.000	807	0.000
10	338	0.000	338	0.000	338	0.000	338	0.000

Table (DO- XVIII)

Dependence of Frequencies and Potential Energy Figures upon the $\gamma(N-N)$ Force Constant. The calculation uses the Force Field Parameters of Table (DO- XVA) Set (II).

$\gamma(N-N)$	0.600		0.500		0.300		0.250	
Number								
1	966	0.013	964	0.010	963	0.006	962	0.006
2	886	0.047	881	0.038	875	0.024	873	0.022
3	790	0.066	783	0.060	773	0.046	771	0.042
4	605	0.265	585	0.286	545	0.252	537	0.227
5	445	0.128	437	0.188	407	0.386	397	0.436
6	275	0.112	270	0.167	252	0.473	243	0.652
7	107	0.035	106	0.051	104	0.147	103	0.215
8	949	0.000	949	0.000	949	0.000	949	0.000
9	785	0.000	785	0.000	785	0.000	785	0.000
10	313	0.000	313	0.000	313	0.000	313	0.000

Table (DO- XIX)

Dependence of the Calculated Non-planar Frequencies upon Non-diagonal Constant f $[\gamma(N-N)/\gamma(C-N)]$. The calculation uses the force constants given in table (DO- XVA) Set (II).

No.	f $[\gamma(N-N)/\gamma(C-N)]$	
	0.050	-0.050
1	966	961
2	885	873
3	788	768
4	579	545
5	419	429
6	255	271
7	104	107
8	949	949
9	785	785
10	313	313

Chapter V.

The vibrational spectra of p-aminophenol and some of its chloro-derivatives have been studied and sets of preferred assignments are given in Table (AP-I). The chief source of ambiguity in the assignments of these spectra is due to the uncertainty concerning the positions of the (N-H) and (O-H) in- and out-of-plane bending vibrations.

p-Aminophenol:

Assuming that the aminophenol molecule is planar then the free species will strictly, belong to the symmetry point group C_s if the hydrogen atom of the (O-H) substituent is ignored however, then it is possible to consider the molecule as having C_{2v} symmetry. In the solid phase extensive hydrogen bonding takes place and the unit cell contains four molecules. The symmetry is therefore quite possibly lower than C_{2v}. The only other aminophenol which possesses a C_{2v} skeleton is 2,6:dichloro p-aminophenol, but the same situation and argument could be applied in this case as in the case of aminophenol itself.

4000-2000 cm^{-1}

The fundamentals expected in this region are (N-H), (O-H) and (C-H) stretching vibrations, the first two are supposed to occur in the region 3400-3600 cm^{-1}. The latter being slightly broader and more intense.

In addition to this two weak absorptions occur at 3040 and 3060 cm^{-1}, in the same spectrum. The first two absorptions are assigned to (O-H) and (N-H) stretches respectively, and the latter to (C-H) stretches. Two more, rather broad bands, with maxima at 2600 and 2692 cm^{-1} are also observed in this region.

2000-1000 cm^{-1}:

Two ν(C-C) modes are assigned to the absorptions at 1620 and 1598 cm^{-1} by Prichard[23], largely on the basis of comparison with the spectra of other para-substituted benzene derivatives. The presence of two medium-weak bands around these wavenumbers is a feature shared by all the other aminophenol molecules considered in this study and their assignment in the same way as for p-aminophenol itself may be consistently retained. Prichard has assigned the symmetric (N-H) bending mode to an absorption at 1626 cm^{-1} which is observed in the solid state spectrum recorded for this study as a weak shoulder band. Deuteration experiments show that the main absorption at 1620 cm^{-1} is sensitive to deuterium exchange.
Two other (N-H) bending vibrations are assigned by Prichard and these are the twisting and wagging modes which are allocated to the broad band at 1155 cm^{-1}. and an absorption at 848 cm^{-1} respectively.

The intense absorption at 1514 cm^{-1} together with the bend at 1475 cm^{-1} are assigned to two more (C-C) stretches by Prichard, the latter absorption is extremely strong and broad and a similar absorption is observed in the spectra of all the chloro derivatives, it behaves upon progressive deuteration as if it were at least partly due to (N-H) or (O-H) bending vibration. The spectrum of the nearly completely deuterated species, however, has a sharp medium intensity band at 1480 cm^{-1}.

The last ν(C-C) mode was assigned by Prichard to an absorption at 1360 cm^{-1}. The only bands which have been observed in this area are the ones at 1389 and 1320 cm^{-1}. The first, which is a broad and moderately intense band, behaves when the compound is deuterated as an(O-H) or (N-H) mode. The second occurs as an extremely weak absorption in the spectrum of the solid, but the spectrum of the deuterated species has a strong absorption at 1318 cm^{-1}. Another infrared absorption which also seems to be sensitive to deuterium exchange is the broad shoulder band at 1220 cm^{-1}. Both this and the 1389 cm^{-1} absorption are allocated to ν(C-C) and β(O-H) modes.

The strong absorptions at 1258 and 1241 cm^{-1} are assigned to (C-N) and ν(C-O) stretching modes and the β(O-H) bending vibrations are assigned to the bands at 1320, 1173, 1097 and 1013 cm^{-1}. Two more absorptions are observed at 1122 and 1155 cm^{-1}. The first is rather weak and may be due to a combination or overtone. The second band is of medium intensity and appears to be sensitive to deuteration, its assignment to a (N-H) bending mode is therefore best retained.

Region 1000-400 cm^{-1}:

The out-of-plane γ(N-H) and γ(O-H) vibrations are reported by Bellamy[24] as usually occuring in the region 900-800 and 700-600 cm^{-1}, respectively. A broad and rather intense absorption occurs at 974 cm^{-1} in the spectrum of the solid mull which may be assigned to one of the (N-H) out-of-plane bends. The ring breathing mode is allocated to either band 974 or 844 cm^{-1} by Prichard[23]. The Raman spectrum contains an extremely strong line at 848 cm^{-1} which has a shoulder band at 807 cm^{-1}.

The main band is assigned to the ring breathing mode. The intense infrared band observed at 754 cm^{-1}, by Prichard was assigned to an(a_1) α(C-C-C) mode, the corresponding Raman line is rather weak and occurs at 750 cm^{-1}. An infrared band at 707 cm^{-1} behaves in the opposite manner being more intense in the Raman effect, this has been assigned as an out-of-plane (C-C) bend. Both of these assignments are retained for the time being. Another infrared absorption at 649 cm^{-1} becomes quite intense in the Raman spectrum this is quite probably an in-plane (C-C) deformation, or γ(O-H) mode. The bands at 476, 527 and 516 cm^{-1} have been assigned as α(C-C-C) a_1; a β(C-N),b_2; and a ϕ(C-C), $b_1$deformation. No Raman shifts are observed in the region 600-500 cm^{-1} but two moderately intense and broad bands occur at 492 and 472 cm^{-1}. The remaining ϕ(C-C) is allocated to the weak absorption at 496 cm^{-1} and the (C-O) bending vibration (in-plane) to the band at 389 in the Raman spectrum. The most suitable assignment of the γ(C-H) deformation appears to be the strong band at 754 cm^{-1}, in other aminophenols and hydroquinones a considerably weaker band in the region 500-750 cm^{-1} is used for the corresponding mode.

This band has already been assigned to an in-plane (C-C) deformation it is not unlikely however that a situation prevails in this region that is similar to the one observed in the higher in-plane and β(N-H) bending regions, where it was found that the number of absorptions exhibiting sensitivity to deuteration (undergoing considerable changes in intensity and/or position) exceeded the number of β(O-H) and β(N-H) modes expected in the region 1100-1500 cm^{-1}.

Only three distinct Raman bands are observed in the region 40-400 cm^{-1}, they occur at 208, 183 and 116 cm^{-1}. The second is a rather doubtful shoulder absorption. The remaining modes left from the higher region are the (C-O) and (C-N) out-of-plane bends, they are allocated to the medium and strong Raman lines at 208 and 116 cm^{-1}. The NCA treatment which is based on a simple Sherer chlorobenzene force field[25] reveals that these modes contain substantial amounts of (C-C) deformation.

Table (AP - I)

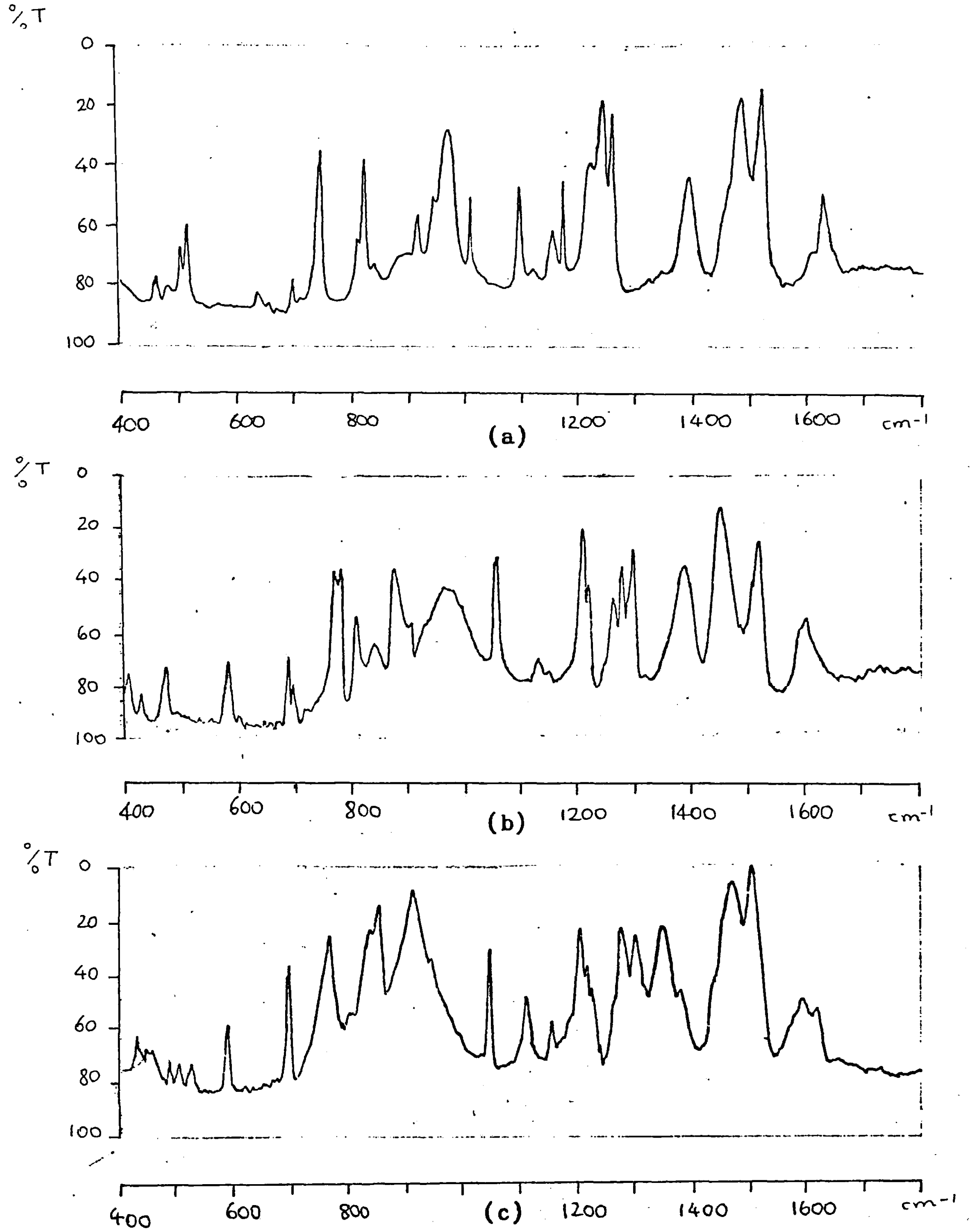
Assignment of the Vibrational Fundamentals of the p-Aminophenols

	AP	2AP	3AP	25AP	26AP
ν(O-H)	3350	3360	3380	3374	3375
ν(N-H)	3292	3296	3300	3292	3310, 3270
ν(C-H)	3060	3048	3025	3060	3058
ν(C-H)	3040				
ν(C-C)	1620	1602	1617	1597	1620
ν(C-C)	1598	1595	1590	1566	1580
ν(C-C)	1514	1518	1504	1496	1492
ν(C-C)	1220	1299	1266	1220	1278
β(N-H)	1620	1616	1617	1607	1590
β(N-H)	1475	1450	1469	1472	1492
β(O-H)	1389	1386	1347	1315	1325
ν(C-N)	1258	1278	1302	1270	1298
ν(C-O)	1241	1209	1202	1204	1225
β(C-H)	1320	1263	1278	1163	1263
β(C-H)	1173	1220	1155	1118	1196
β(C-H)	1097	1054	1110		
β(C-H)	1013				
ν(C-Cl)		1057	1045	1076	1185
ν(C-Cl)				865	847
RB	848	785	750	805	795
α(C-C-C)	649	693	695	650	709
α(C-C-C)	516	589	502, 587	559, 584	505, 613
α(C-C-C)	476	438	457	483	383
β(C-N)	527	482	487	500	590
β(C-O)	389	417		428	431
β(C-Cl)		264	433		
β(C-Cl)					
γ(N-H)	1155	1129	1155	1155	1140
γ(N-H)	974	954	914	912	904
γ(O-H)	754	776	765	584, 559	613
γ(C-H)	949	908	940	997	960
γ(C-H)	923	878	853	845	806
γ(C-H)	830	811	836		
γ(C-H)	820				
ϕ(C-C)	754	703	502, 587	710	601
ϕ(C-C)	707	584	524	524	458
ϕ(C-C)	496	374	433		
γ(C-N)	268	346		160	228
γ(C-O)	116	106		144	106
γ(C-Cl)					228
γ(C-Cl)					

Table (AP- II)

Observed Spectra of some p-Aminophenols

p-Aminophenol		2:Chloro p-Aminophenol		3:Chloro p-Aminophenol	
Infrared * ‡	Raman * ‡	Infrared * ‡	Raman * ‡	Infrared * ‡	Raman * ‡
3350 (32)		3360 (30)		3380 (42)	
3292 (34)		3296 (36)		3300 (34)	
3060 (5)		3208 (6)b			
3040 (7)		3048 (5)b		3025 (1)	
2692 (9)		1602 (20)	1624 w		
2600 (10)		1595 (18)	1608 w	2785 (50)b	
1626 (5)	1624 mw	1518 (55)	1520 vw	2660 (50)b	
1620 (23)		1506 (42)sh			
1598 (12)		1450 (60)	1440 vw		
1514 (66)		1386 (40)		1617 (17)	
1480 (62)		1299 (43)	1288 wm	1590 (19)	
1389 (30)		1278 (38)		1504 (65)	
1342 (5)		1263 (27)		1437 (40)	
1320 (4)		1220 (56)sh	1224 vw	1347 (41)	
1258 (57)		1209 (50)		1320 (4)sh ?	
1241 (62)	1242 w,sh	1129 (7)	1148 vw	1302 (5)?	
1220 (40)sh		1057 (42)		1278 (20)sh b	
1173 (24)		1054 (40)sh	1052 vw	1238 (5)sh	
1155 (18)	1152 w	954 (25,6)		1224 (24)sh	
1122 (4)		908 (11)sh	910 vvs	1214 (24)sh	
1097 (33)		878 (33)		1202 (46)	
1013 (30)		844 (7)b	848 vw	1155 (15)	
974 (52)	974 w	811 (27)		1110 (26)	
	970 vw	785 (46)		1045 (33)	
949 (20)sh		776 (46)	774 vvs		
923 (14)		703 (12)	704 vw sh		
848 (7)	848 vs	693 (22)	692 vvs	940 (32)	
830 (49)		589 (12)	560 vw	914 (54)	
820 (20) sh	807 w	482 (14)	490 wm	852 (40)	
754 (50)	750 vw	438 (1)	480 w,sh	836 (30)	
707 (10)	707 w	417} (1)d	415 w	765 (49)b	
669 (6)		414}		695 (40)	
649 (6)	651 w		374 w	750 (20)	
527 (26)			346 w	587 (21)	
516 (20)			268 m	524 (6)	
496 (6)	492 w		264 m,sh	502 (6)	
476 (8)	472 w		230 w	487 (7)	
408 (7)b			185 wm	457 (10)	
	389 vw		106 w,sh	464 (11)	
	368 vw		u.r.	433 (13)	
	208 w				
	183 w				
	116 vw				



Infrared spectra for (a) para aminophenol, (b) 2:chloro para aminophenol and (c) 3:chloro para aminophenol.

2:Chloro p-aminophenol:

This molecule belongs to the point group C_s, all the fundamental vibrations should therefore be active in the Raman and infrared.

4000-2000 cm^{-1}:

Three absorptions are observed at 3360, 3296 and 3208 cm^{-1}. The latter being very broad and rather weak, the first two are allocated to the (O-H) and (N-H) stretching vibrations respectively. The third band probably arises from intramolecularly hydrogen bonded (O-H) and (N-H) vibrations. A similar absorption is barely visible in the infrared spectrum of aminophenol at 3200 cm^{-1}. The (C-H) stretching vibrations give rise to a very weak band at 3048 cm^{-1}.

2000-1000 cm^{-1}:

The two highest ν(C-C) modes are assigned to the bands at 1602 and 1595 cm^{-1}, both are weak absorptions and very similar to the ones observed in the case of p-aminophenol, the latter band being a rather poorly defined shoulder absorption. The Raman spectrum contains a broad and complex pattern having a maximum at 1624 cm^{-1} this possibly corresponds to the similar p-aminophenol band which was assigned by Prichard to a (N-H) in-plane deformation.

Another (C-C) stretching mode is assigned to the band at 1518 cm^{-1} the shoulder band which is found at 1506 cm^{-1} probably arises from a splitting imposed by the crystal structure. The broad and strong band observed at 1450 cm^{-1} is assigned to a (N-H) in-plane bending mode as well as a (C-C) stretching vibration, and the one at 1386 cm^{-1} is allocated to a β(O-H)/ ν(C-C) mode. Three absorptions are observed in the region 1200-1300 cm^{-1}. The highest of the three at 1299 is assigned to the (C-N) mode and the remaining two at 1278 and 1263 cm^{-1} to a (C-H) and ν(C-C) / β(O-H) vibration, respectively.

The medium and strong absorptions at 1220 and 1209 cm^{-1} are allocated to β(C-H) and ν(C-O) modes respectively. The band at 1129 cm^{-1} probably involves (N-H_2) deformation vibration. A relatively strong band is observed at 1057 cm^{-1} with a shoulder at 1054 cm^{-1} they are assigned to a ν(C-Cl) and β(C-H) mode respectively. The corresponding assignments for 2:chloro-parahydroquinone in this region are very similar to the ones just outlined.

The only intense Raman line in the region 2000-1000 cm^{-1} is the one at 1288 cm^{-1} other medium or weak Raman lines are observed at 1624, 1224, 1148 and 1052 cm^{-1}.

1000-400 cm^{-1}:

The broad band at 954 cm^{-1} in the infrared spectrum is assigned to an out-of-plane (N-H) bending mode. A shoulder absorption appears at 908 cm^{-1} in the infrared, which occurs with a very high intensity in the Raman spectrum it is assigned to an out-of-plane (C-H) bending mode. The ring breathing mode should occur in the region 900-750 cm^{-1}, from comparison with the other aminophenols and hydroquinones this mode is expected to give rise to a somewhat intense band in the Raman spectrum, such a band is observed at 785 cm^{-1} in the infrared and 774 cm^{-1} in the Raman, the infrared absorption is accompanied by an equally intense band at 776 cm^{-1}. This is possibly due to a splitting caused by the crystal structure.

The other out-of-plane (C-H) bends are assigned to the bands at 878 and 811 cm^{-1} both give rise to medium-weak absorptions in the infrared and very weak lines in the Raman effect. A broad and rather weak band occurs at 844 cm^{-1} in both the infrared and Raman, it is quite probably due to a combination or overtone (e.g. $589 + 268 = 859\ cm^{-1}$; $417 \times 2 = 834\ cm^{-1}$). Its shape however suggests that it may be involved in (N-H) or (O-H) out-of-plane bending vibrations. Further discussion of this assignment as well as the one concerning the absorption at 776 cm^{-1} is to be made towards the end of this section.

The highest out-of-plane (C-C) deformation is assigned to the band at 703 cm^{-1} and the in-plane (C-C) bend to the absorption at 693 cm^{-1} in the infrared and an extremely intense band around this position in the Raman spectrum. The region 700-500 cm^{-1} may be expected to contain the out-of-plane (O-H) deformation the only absorptions met in this region, however, are the bands at 589 and 584 cm^{-1} in the infrared and the weak Raman band at 560 cm^{-1}. The main absorption at 589 cm^{-1} is much sharper than might be expected for this assignment, alternative assignments for it may be in-plane or out-of-plane (C-C) deformations, both assignments are supported by the preliminary NCA which uses a simple 47-parameter benzene type force field, the absorptions at 589 and 584 cm^{-1} are therefore provisionally allocated to these modes.

The out-of-plane (O-H) deformation which is now left to be assigned outside the range found for the other substituted aminophenols is probably best assigned to the relatively broad band at 776 cm^{-1}, which was previously, provisionally, assigned as part of a doublet absorption connected with the ring breathing vibration. This assignment is similar to the one made for aminophenol. The remaining bands at 482, 438 and 417 cm^{-1} are assigned as (C-N), (C-C) and (C-O) in-plane bending vibrations.

400-40 cm^{-1}:

Only one out-of-plane (C-C) deformation is left to be assigned in this region it is allocated to the absorption at 374 cm^{-1}. The bands at 346 and 185 are assigned to (C-N) and (C-O) out-of-plane bends and the absorptions at 264 and 106 are probably best attributed to in-plane and out-of-plane (C-Cl) bending vibrations.

3:Chloro p-aminophenol:

4000-2000 cm^{-1}:

The (N-H) and (O-H) stretching vibrations are assigned to the absorptions at 3300 and 3380 cm^{-1} respectively. An unresolved shoulder absorption is associated with the former band this is perhaps to be expected in view of the possibility of intra-molecular H-bonding. In addition to this, two extremely broad absorptions are observed in the infrared spectrum which have diffuse maxima around 2785 and 2660 cm^{-1}. The (C-H) modes give rise to only one noticeable absorption at 3025 cm^{-1}. The fact that even thick mulls could not be made to produce a reasonably strong absorption in the region 3000-3100 cm^{-1} is due to the broad absorptions at 2800 cm^{-1} which tail off beyond this region.

2000-1000 cm^{-1}:

The three highest ν(C-C) absorptions are observed at 1617, 1590 and 1504 cm^{-1} analogous with the corresponding assignments of p-aminophenol and 2:chloro- p-aminophenol. The intense absorption at 1469 cm^{-1} is also assigned to a ν(C-C) stretching mode with a high percentage of ($N-H_2$) in-plane deformation. This absorption has a shoulder peak at 1437 cm^{-1} which is assigned to a ν(C-C) mode. A broad and rather strong band is observed at 1347 cm^{-1} which is allocated to the in-plane (O-H) deformation and the lowest ν(C-C) stretching mode in accordance with the similar assignment for the other aminophenols and with the results of the deuterium exchange studies. The absorption at 1278 cm^{-1} is assigned to a β(C-H) mode and the bands at 1302 and 1202 cm^{-1} to ν(C-N) and ν(C-O) stretching vibrations. The latter absorption has shoulder bands at 1214 and 1224 cm^{-1} one of these is possibly a combination absorption (e.g. 695 + 524 = 1219, 765 + 457 = 1222, 756 + 634 = 1229 cm^{-1}). The remaining absorption is, however, probably due to another β(C-H) mode. The intense-medium band observed at 1045 cm^{-1} is assigned to the (C-Cl) stretching vibration. This leaves two bands at 1110 and 1155 cm^{-1} which are assigned to a (C-H) and a (N-H) bending mode, respectively. This set of assignments is preferred to other possible ones since it is supported by the results of the preliminary NCA.

Region 1000-400 cm^{-1}:

The broad and strong band at 914 cm^{-1} is readily allocated to an out-of-plane (N-H) deformation vibration, its shoulder band which has a maximum at 940 cm^{-1} is assigned to a γ(C-H) deformation. Two other (C-H) out-of-plane bends are provisionally assigned to the absorptions at 852 and 836 cm^{-1}. The latter is a broad band which could possibly be assigned as another (N-H) or (O-H) out-of-plane deformation in a manner similar to the analogous absorption in the case of 2:chloro p-aminophenol; the first assignment will, nevertheless, be retained for the time being. The broad strong-medium absorption at 765 cm^{-1} has a resolved shoulder absorption at 750 cm^{-1}.

The main absorption is assigned to the (O-H) out-of-plane bend and the medium intensity shoulder band to the ring breathing mode, the sharp and medium intensity band at 695 cm^{-1} is probably best assigned to an in-plane (C-C) bending vibration, and the less intense band at 502 cm^{-1} to an out-of-plane (C-C) bending mode, the remaining assignments in this region are given in table AP-I .

25:Dichloro p-aminophenol:

4000-2000 cm^{-1}:

The (C-H) stretching absorptions are too weak to be observed even when very thick mulls are used. The (N-H) and (O-H) stretching vibrations give rise to two strong and narrow bands at 3292 and 3374 cm^{-1} respectively. The band shapes and intensities resemble those observed in the cases of p-aminophenol, 2:chloro aminophenol and 3:chloro aminophenol. A broad absorption with a maximum at 2600 cm^{-1} is also observed in this region.

2000-1000 cm^{-1}:

The first four (C-C) stretching vibrations are assigned to the bands at 1597, 1566, 1496 and 1427 cm^{-1}. The (N-H) and (O-H) in-plane bends are allocated to the absorptions at 1472 and 1315 cm^{-1}, respectively. Both are strong and broad and resemble the corresponding absorptions in aminophenol, 2:chloro aminophenol and 3:chloro aminophenol. Another relatively broad absorption is observed at 1270 cm^{-1}. This also appears to be rather sensitive to deuteration; it is allocated to the (C-N) stretching mode. The band at 1220 cm^{-1} is too weak to be assigned to the (C-O) stretch expected in this region, instead the absorptions at 1204 and 1155 cm^{-1} appear better suited for this assignment. The latter is a broad band with a somewhat ill-defined shoulder absorption, it is likely that it involves (O-H) or (N-H) deformation vibrations.

The bands at 1220 and 1204 cm^{-1} are assigned to the ν(C-O) / β(O-H) and ν(C-O) modes respectively. The modes which remain to be assigned in this region are the two β(C-H) and one ν(C-Cl) vibration; the NCA treatment shows that the (C-Cl) stretching character is distributed among the modes in the range 1200-850 cm^{-1}. The ones with the highest share of ν(C-Cl) contribution are at 1076 and 865 cm^{-1}. The (C-H) bending modes are assigned to the band at 1163 and 1118 cm^{-1}.

1000-400 cm^{-1}:

A weak absorption is observed at 997 cm^{-1}; this is quite possibly due to a γ(C-H) mode. The broad band at 912 cm^{-1} resembles very closely the absorptions of p-aminophenol, 2:chloro p-aminophenol and 3:chloro p-aminophenol in the same region, and it is similarly assigned to the γ(N-H) mode. Another γ(C-H) vibration is assigned to the medium intensity band at 845 cm^{-1}. A strong absorption occurs at 805 cm^{-1}, this is possibly best assigned as a ring breathing mode. The weak band at 710 cm^{-1} is assigned to a α(C-C-C)/ν(C-Cl) mode and the stronger absorption at 650 cm^{-1} to a α(C-C-C) one. At least one of the β(C-X) modes is expected in this region. The β(C-N) in-plane bend is assigned to the absorption at 500 cm^{-1}, this assignment is supported by the preliminary NCA which predicts such a bending mode at 511 cm^{-1}. The out-of-plane (O-H) vibration occurs in the region 750-500 cm^{-1} in the other aminophenols and in substituted phenols. A weak band at 559 cm^{-1} is allocated to this mode, and the absorptions at 584 and 524 cm^{-1} to α(C-C-C) and ϕ(C-C) modes respectively.

Two weak bands are observed at 483 and 428 cm^{-1}. They are provisionally assigned to α(C-C-C) and β(C-O) modes, respectively.

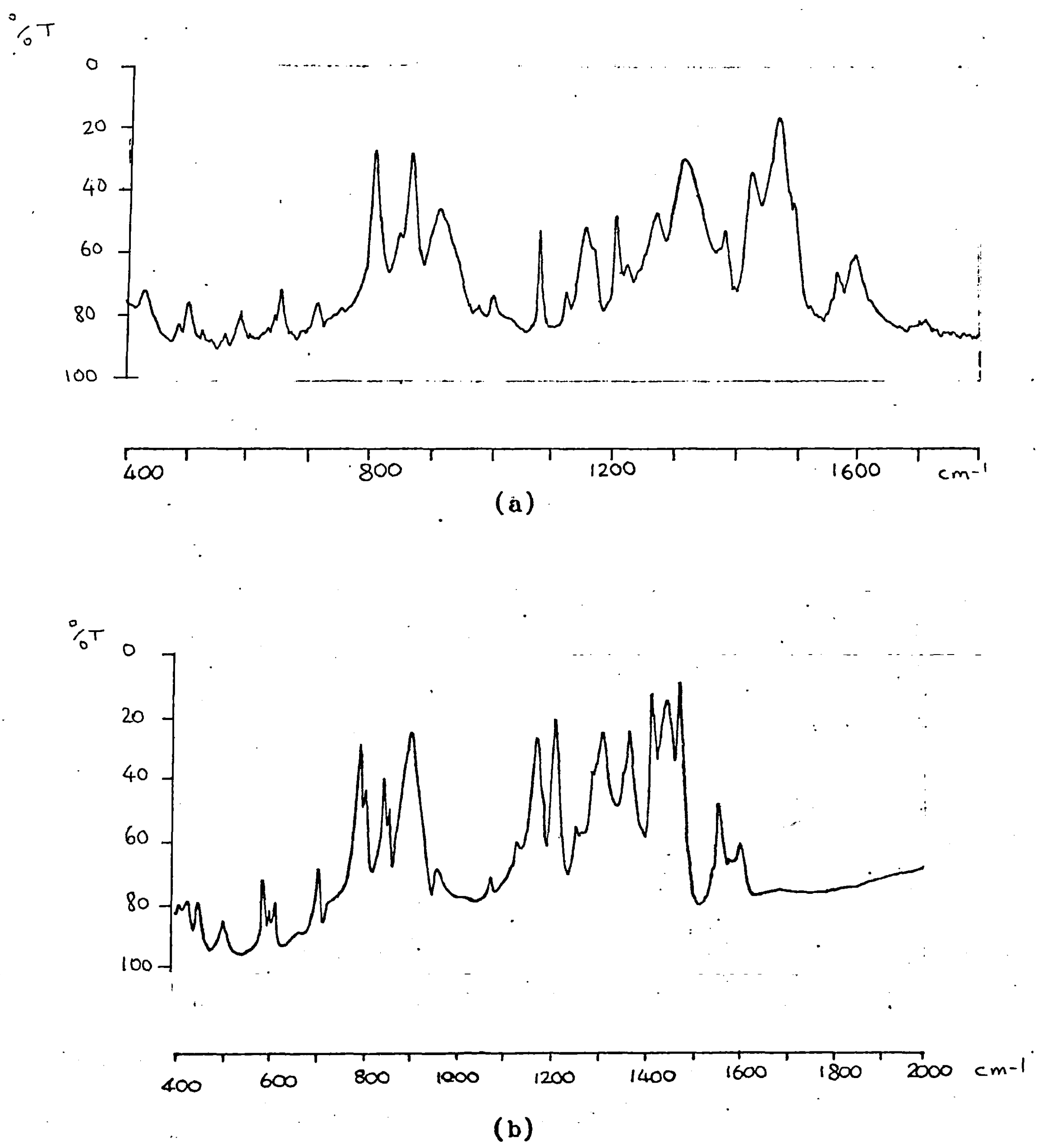
Table (AP- III)

Observed Spectra of 2,5:Dichloro (1) and 2,6:Dichloro p-Aminophenol (2)**

3374 (52)
3292 (49)
2600 (30)
1607 (21)
1597 (22)
1566 (15)
1496 (36)
1472 (63)
1427 (63)
1315 (41)
1270 (21)
1220 (77)
1204 (30)
1163 (20) sh
1155 (30)
1118 (11)
1076 (31)
997 (77)
912 (35)
865 (52)
845 (12)
805 (53)
710 (9)
650 (14)
640 (5) sh
584 (12)
559 (3)
524 (2)
500 (12)
483 (7)
428 (17)

3375 (26)
3310 (24)
3270 (22)
3170 (3)
3058 (6)
2640 (20) vb
2320 (4) b
1620 (14)
1590 (12), b, sh
1580 (19)
1492 (44)
1436 (40)
1325 (30)
1298 (20)
1278 (10)
1263 (9)
1225 (32)
1216 (29)
1196 (27)
1185 (28)
1140 (12)
1080 (3)
975 (12) shur
960 (11)
904 (41)
859 (20)
847 (25)
806 (25)
795 (30)
725 (10) sh?
709 (14)
613 (10)
601 (8) sh
590 (10)
505 (6)
458 (12)
431 (13)
412 (9)

*cm^{-1}
I relative intensity
** nujol mull spectra.



Infrared spectra of (a) 2,5:dichloro para-aminophenol and (b) 2,6:dichloro para-aminophenol.

2,6:Dichloro p-aminophenol:

4000 - 2000 cm^{-1}:

The (O-H) stretching mode is assigned to the intense absorption at 3375 cm^{-1}, and the (N-H) stretching modes are allocated to the bands at 3310 and 3270 cm^{-1}. The spectra of p-aminophenol 2:chloro p-aminophenol, 3:chloro p-aminophenol, and 2,5:dichloro p-aminophenol contain only two major absorptions in this region. The presence of two bands due to the (N-H) stretching vibrations rather than one as in the case of the remaining aminophenols, is probably due to two different and somewhat distinct environments for the (NH_2) group. The spectrum of 2,6:dichloro p-aminophenol hydrochloride contains a medium absorption at 3280 cm^{-1} in addition to a very broad absorption extending over a range of some 500 cm^{-1}. Another feature in this region, which is also present in the spectrum of 2:chloro p-aminophenol is the occurance of a rather weak and broad absorption around 3170 cm^{-1}, this is probably due to intramolecularly hydrogen-bonded (O-H) species.

The (C-H) stretching absorptions are partly obscured by the broad absorptions in this region, nevertheless a weak band is observed at 3058 cm^{-1}.

2000-1000 cm^{-1}:

Four of the (C-C) stretching modes are assigned to the absorptions at 1620, 1580, 1492 and 1436 cm^{-1}. These assignments are the most consistent with those made for the other aminophenols.

The absorptions at 1590 cm^{-1} is assigned to a (N-H) bending mode.

As with the other aminophenols this absorption could almost certainly be expected to have a considerable amount of (C-C) stretching and (C-H) bending character. The second (N-H) bending mode occurs in the region 1450-1490 cm^{-1} in the remaining aminophenols, only one band of suitable intensity is found here. However, this is the one at 1492 cm^{-1} which has already been assigned to a (C-C) stretching vibration. A double assignment for this absorption is therefore assumed. It should probably be mentioned here that a similar situation was encountered in the case of p-aminophenol itself.

The broad and medium intensity absorption at 1325 cm^{-1} is assigned to the β(O-H)/ν(C-C) mode. The two stretches ν(C-O) and ν(C-N) are expected in the region 1300-1250 cm^{-1}, the only two bands with suitable intensities for these assignments are those at 1298 and 1225 cm^{-1}. The first is provisionally assigned to a (C-N) stretching vibration and the second to the ν(C-O) mode, and the band at 1278 cm^{-1} is allocated to a ν(C-C) mode. The weak absorption at 1263 cm^{-1} is probably another fundamental vibration; if it is so, then it is probably best assigned to a β(C-H) mode. The assignments of the modes left in this region are listed in table AP-I.

Region 1000-400 cm^{-1}:

The Raman spectrum of 2,6:dichloro p-aminophenol has been recorded, but it is of a rather poor quality due to the flourescent nature of the solid. The spectrum does reveal, however, that the weak infrared absorption at 953 cm^{-1} is most probably a fundamental absorption. The infrared spectrum of 2,6:dichloro p-aminophenol in this region contains a broad and rather intense band at 904 cm^{-1} which is assigned as in the spectra of the other aminophenols to a γ(N-H) mode.

The other modes expected to give rise to absorptions in this region are a b_1 (C-H) bend, the ring breathing mode, together with in-plane (C-C), (C-N) and (C-O) bends as well as (C-C) modes. Apart from the intense band at 809 cm^{-1} the only absorptions which could be possibly be allocated to the (C-H) mode (b_1) are the weak band at 795 cm^{-1} and the extremely weak absorptions at 936 and 891 cm^{-1}: The strong band at 809 cm^{-1} is chosen for this assignment which frequently corresponds to an intense infrared absorption. The shoulder absorption at 795 cm^{-1} is assigned to the ring breathing mode, and the rather weak band at 726 cm^{-1} in the infrared is allocated to an (C-C-C) mode. The remaining assignments, which do not require further discussion, are listed in table (AP-I).

Table (AP-IV)

Combination Bands of p-Aminophenol

Observed	Combination	Difference
2692	1598 + 1097 = 2695	3
	1514 + 1173 = 2687	5
	1475 + 1220 = 2695	3
2600	3350 - 754 = 2596	4
	1620 + 974 = 2594	6
	1220 + 1389 = 2609	9
1514	1514 + 116 = 1630	4
	1155 + 476 = 1631	5
	517 + 1097 = 1624	2
	389 + 1241 = 1630	4
	974 + 649 = 1623	3
	923 + 707 = 1630	4
1389	1514 - 116 = 1398	9
	923 + 476 = 1399	10
1342	1220 + 116 = 1336	6
	527 + 820 = 1347	5
	389 + 949 = 1338	4
	830 + 516 = 1346	4
1122	1598 - 476 = 1122	0
	1514 - 389 = 1125	3
	1389 - 268 = 1121	1
	476 + 649 = 1125	3
	1013 + 116 = 1128	7
	848 + 268 = 1116	6

Observed	Combination	Difference
669	1620 - 949 = 671	2
	1320 - 649 = 671	2
496	974 - 476 = 498	2
	1320 - 830 = 490	6
	1320 - 820 = 500	4
	1013 - 516 = 497	1
408	527 - 116 = 411	3
	923 - 516 = 407	1
	1258 - 848 = 410	2
	1241 - 830 = 411	3
268	1220 - 954 = 266	2
	1054 - 785 = 269	1
	1148 - 878 = 270	2
	703 - 438 = 265	3
	374 - 106 = 268	0
264	1220 - 954 = 266	2
	954 - 693 = 261	3
	703 - 438 = 265	1
	374 - 106 = 268	4
230	1450 - 1220 = 230	0
	1616 - 1386 = 230	0
	811 - 584 = 227	3
185	1450 - 1263 = 187	2
	1057 - 878 = 179	6
	1148 - 954 = 194	9
	776 - 589 = 187	2
	878 - 693 = 185	0

2:Chloro p-Aminophenol

1209	785	+	417	=	1202	7
	776	+	438	=	1214	5
	954	+	264	=	1218	9
1129	1616	-	482	=	1134	5
	1386	-	264	=	1122	7
	785	+	346	=	1131	2
	693	+	438	=	1131	2
	703	+	417	=	1120	9
	776	+	346	=	1122	7
844	1616	-	776	=	830	4
	1278	-	438	=	840	4
	1263	-	417	=	846	2
	589	+	264	=	853	9
	417	x	2	=	834	10
584	1278	-	693	=	585	1
	693	-	106	=	587	3
	482	+	106	=	588	4

2,5:Dichloro p-Aminophenol

2600	1597	+	997	=	2594	6
	1427	+	1163	=	2590	10
	1607	+	997	=	2604	4
	1472	+	1118	=	2590	10
1163	1597	-	428	=	1169	6
	584	x	2	=	1168	5
	997	+	160	=	1157	6

640	1163 - 524 = 639	1
	1220 - 584 = 636	4
	483 + 160 = 643	3
	500 + 144 = 644	4
559	1427 - 865 = 562	3
	1472 - 912 = 560	1
	1270 - 710 = 560	1
	1118 - 559 = 559	0
524	1597 - 1076 = 521	3
	1607 - 1076 = 531	7
	1076 - 559 = 517	7
	1115 - 584 = 531	7

3:Chloro p-Aminophenol

2785	1590 + 1202 = 2792	7
	1504 + 1278 = 2782	3
	1437 + 1317 = 2784	1
2660	1617 + 1045 = 2662	2
	1504 + 1155 = 2659	1
1320	487 + 836 = 1323	3
1224	695 + 524 = 1219	5
	457 + 765 = 1222	2
1214	750 + 457 = 1207	7
	695 + 524 = 1219	5
	457 + 765 = 1222	8
765	1617 - 852 = 765	0
	1266 - 502 = 764	1

502	1266 - 765 = 501	1
464	1617 - 1155 = 462	2
	1504 - 1045 = 459	5
	1302 - 836 = 466	2
	1155 - 695 = 460	4

Normal Co-ordinate Treatment of some p-Aminophenol Molecules

Two types of force fields were used in calculating the planar vibrational frequencies of the p-aminophenols; these sets differ from one another by the introduction of additional force constants to distinguish between cross terms involving different co-ordinates such as β(C-O) and β(C-H), for example; and also by distinguishing different types of the same co-ordinate - e.g. α(1) and α(2). Examples of these sets of force constants for p-aminophenol itself together with the corresponding frequencies are given in table (AP- V).

The same force field was used with the chloro- derivatives, with the additional ν(C-Cl) and β(C-Cl) diagonal constants, which were equated to 3.9×10^5 dyne cm^{-1} and 1.2×10^{-11} erg respectively, and the interaction constants involving (C-Cl) vibrations which were transferred from similar quinones. The values of the other diagonal parameters which differ from those used in the corresponding quinones and the additional (N-H) and (O-H) constants are given in table (AP-VI).

Table (AP-VII) contains several sets of frequencies calculated for p-aminophenol by allowing a number of force field parameters from set II of table (AP-V) to vary one at a time. The calculated frequencies are accompanied by numbers expressing the contribution of the variable force constant to that particular frequency.

Table (AP - VIII) contains the calculated frequencies of some of the compounds considered in this study, it may be immediately seen that the highest frequencies below 2000 cm^{-1} are too high. This is thought to be primarily due to the fact that the interaction between (N-H) bending and (C-C) stretching co-ordinates was not taken into account.

Considerable improvement in the fit between calculated and assumed frequencies is obtained when these constants are taken into account and also when the (O-H) bending interactions with other modes are included. It is doubtful, however, whether this improvement is of real significance since the symmetries of the infrared absorptions cannot be established with certainty. A set of possible (N-H) and (O-H) stretching and bending parameters are given in table (AP - VI).

The non-planar vibrations of p-aminophenol and its chloro-derivatives have been calculated using the potential energy parameters listed in tables (AP - IX and X), the first contains parameters appropriate to the parent compound while the latter gives those for the 2,6:dichloro derivative as an example of the type of parameters used with the chloro derivatives. The features exhibited by the potential energy distribution for the parent compound are charecteristic of all the aminophenols considered here. Table (AP-XI) gives an idea of the dependence of the calculated frequencies upon the diagonal force constants.

The Cartesian displacement figures for 2,6:dichloro p-aminophenol, given in table (AP-XII), were calculated from the set of force field parameters listed in table (AP- X).

Table (AP- VA)

Force Constants Used in Calculating the Planar Vibrations of p-Aminophenol

Number	Description	I		II
1	101	2.0816	101	2.2873
2	102	0.3400	202	2.3000
3	108	-0.1057	102	0.4553
4	213	-0.2890	208	0.0000
5	119	-0.3166	108	-0.1877
6	707	1.8365	109	0.0000
7	1010	1.8365	107	0.0000
8	808	1.0174	207	0.0000
9	708	-0.2934	307	0.0000
10	709	-0.1715	119	-0.5003
11	710	0.0943	219	0.0000
12	713	-0.2545	113	-0.2515
13	714	-0.0225	214	-0.2515
14	819	-0.2901	114	0.0000
15	1222	-0.0847	115	0.0000
16	1313	6.2000	707	2.4086
17	1414	6.2000	1010	2.4086
18	1314	0.8595	710	-0.0179
19	1315	-0.6133	708	0.0193
20	1316	-0.0479	769	-0.0153
21	1317	-0.0117	713	-0.0545
22	1318	0.2678	714	0.0534
23	1319	0.8466	808	1.0171
24	1322	0.1711	809	0.0193
25	1417	0.9911	812	-0.0153
26	1419	-0.1786	812	-0.0179
27	1919	5.6066	811	-0.4983
28	2222	6.1485	819	0.0600
29	2020	4.9944	822	0.0545
30	2021	0.0533	814	0.0545
31	2024	-0.0400	815	0.0545
32	2023	0.0080	1313	6.2000
33	2525	6.0856	1914	6.2000
34	2727	6.0429	1314	0.8325
35	2526	0.1024	1318	0.6760
36	2828	1.2134	1315	-0.9750
37	3030	1.2829	1317	-0.0688
38			1316	-0.0696
39			1417	0.0280
40			1319	0.8900
41			1419	-0.2180
42			1322	0.3153

Table (AP- VA)Cont.

43	1919	4.8800
44	2222	4.4855
45	1922	0.0000
46	2020	5.0930
47	2021	0.0250
48	2024	-0.0400
49	2023	0.0080
50	2525	6.0000
51	2626	6.0000
52	2526	0.1024
53	2727	1.0000
54	2828	0.8859

Table (AP- VB) Cont.

Calculated Planar Frequencies of p-Aminophenol

	Set (I)		Set (II)	
1	3352	1	3354	1
2	3293	2	3281	2
3	3293	2	3241	2
4	3063	3	3084	3
5	3050	3	3078	3
6	3032	3	3063	3
7	3003	3	3045	3
8	1791	4/6/7	1774	4/7/6/5
9	1685	7/6/4/5	1577	4/7/6/5
10	1665	4	1526	4/5/7
11	1563	4/7/6	1519	4/5
12	1508	4	1423	7/6/5/10/9
13	1405	4/7/6	1360	7/6/5/10/9
14	1381	4/5	1337	9/10/5/6
15	1363	7/6/5	1300	6/5/7
16	1299	4	1249	9/6
17	1291	5/7/4	1205	7/5
18	1229	9/10/7	1190	5/7/6
19	1142	5	1108	5/8
20	1005	5	1031	8/5
21	983	5	952	8/5/9
22	825	8/5	797	4/8
23	711	8	774	8/4
24	643	8	665	8
25	454	8	497	8/11
26	389	11	440	12/8
27	310	12	345	11/12

1: ν(O-H); 2: ν(N-H); 3: ν(C-H); 4: ν(C-C); 5: β(C-H);
6: β(O-H); 7: β(N-H); 8: α(C-C-C); 9: ν(C-O); 10: ν(C-N);
11: β(C-O); 12: β(C-N); 13: ν(C-Cl); 14: β(C-Cl).

Table AP VI

Summary of (N-H) and (O-H) force field parameters and calculated frequencies for p-Aminophenol

1	ν O-H	5.500	6.000	6.000	6.042
2	ν N-H	4.500	6.000	6.000	6.085
3	ν N-H/ ν N-H	0.000	0.000	0.000	0.102
4	β O-H	2.880	0.885	0.800	1.213
5	β N-H	2.300	1.085	0.880	1.283
6	β N-H/ β N-H	0.000	0.000	0.000	0.000
7	ν C-O	3.500	5.000	4.880	4.806
8	ν C-N	3.500	5.000	4.485	4.248
9	ν C-C	0.900	6.003	6.200	6.200
10	β C-H	1.017	1.017	1.017	1.017

Calculated N-H and O-H stretches

3823	3352	3354	3352
2937	3293	3281	3293
2659	3293	3241	3293

Table (AP- VII)

Calculated Planar Fundamentals of p-Aminophenol

Parameter: 53=1.0000 54 = 0.8859 43 = 6.7881 44 = 5.0686

1	3357	PED*	3357	PED	3357	PED	3357	PED
2	3281		3281		3282		3282	
3	3242		3242		3242		3242	
4	3084		3084		3084		3048	
5	3078		3078		3078		3078	
6	3064		3064		3064		3064	
7	3046		3046		3046		3046	
8	1800	0.17	1800	0.02	1800		1800	
9	1615	0.25	1615	0.10	1616		1616	
10	1545	0.15	1545		1546	0.01	1548	0.03
11	1522	0.10	1522		1523		1523	
12	1470	0.27	1470		1472	0.24	1477	0.10
13	1438	0.63	1438		1469	0.19	1469	
14	1381	0.09	1382	0.32	1425	0.10	1429	0.05
15	1333	0.05	1333		1361	0.02	1361	0.04
16	1291	0.13	1291	0.06	1291		1305	0.22
17	1285	0.12	1285	0.01	1288		1290	
18	1228	0.05	1230	0.43	1231		1231	0.02
19	1109		1109		1109		1109	0.03
20	1055		1055		1069	0.13	1096	0.05
21	958		958		995	0.22	1013	0.31
22	808		808		822		823	0.04
23	676		676		7090	0.14	719	0.46
24	670		670		673		673	
25	498		498		498		498	
26	454		454		462	0.13	466	0.13
27	345		345		345		345	
	41.1		40.9		37.0		35.6	

* These figures refer to contributions made by the force constants given above; the numbers preceeding the values of the force constants are the serial numbers of table (AP - VA).

Table (AP- VII)Cont.

Parameter 32=6.3000 33 = 6.5279

3357	PED	3257	PED
3282		3282	
3242		3242	
3083		3085	
3077		3078	
3066		3065	
3045		3046	
1719	0.40	1808	
1590	0.14	1624	0.15
1538	0.05	1567	0.49
1508	0.04	1529	0.05
1542	0.13	1489	0.40
1431	0.30	1479	0.03
1413	0.13	1436	0.12
1340	0.09	1365	0.03
1288	0.14	1307	0.02
1275	0.08	1292	
1176	0.39	1235	
1071	0.60	1119	0.28
1061		1070	
993		1017	0.08
764		828	
716		719	
655		674	
495		498	
464		469	0.25
340		346	0.03
41.6		35.0	

Table (AP VIII)

Calculated Planar Fundamentals of some Chloro para-Aminophenols

	3AP				25AP			
		(N-H)	(O-H)			(N-H)	(O-H)	
1	3397			3	3387			1
2	3282			2	3374			2
3	3281			2	3273			2
4	3079			1	3067			3
5	3069			1	3067			3
6	3054			1	1747	0.05	0.03	4
7	1753	0.05	0.01	4	1616	0.09	0.03	4/7/5/8
8	1570	0.01		4/5	1567	0.02	0.02	4/5
9	1553	0.04	0.02	4	1414	0.13	0.13	4/7/9/10
10	1488	0.07	0.11	4/6	1443	0.16	0.15	7/6/4
11	1427	0.12	0.01	7/4	1356	0.25	0.05	7/9/10
12	1401	0.30		7/5/4	1289	0.51	0.42	6/7/5/4
13	1367	0.31	0.08	7/9	1256	0.28	0.02	5/9/10/7
14	1317	0.23	0.13	4/5/7/6	1208	0.24	0.04	13/7/6/8/9
15	1276	0.03	0.06	5/9/10	1188	0.04	0.03	13/5/4
16	1235	0.34	0.32	7/6	1168	0.02	0.03	3/6/8
17	1150	0.29	0.20	5/7/6/13	1122	0.10	0.01	13/8/5/7
18	1129	0.10	0.05	5/7	1993	0.03		10/9/13
19	1093	0.10		13/7/8	803	0.02		4/8
20	886	0.02		8/13/4	737			8/13/4
21	758			8/11	533			8/14/11
22	718	0.19		8/12/14	515			8/12
23	493	0.08		8	471			8
24	480	0.06		12/14	310			12/14
25	426				285			
26	294			11/12/14	202			14/11/12
27	193	0.03		14	175			14

Table (AP-IX)

Non-Planar Force Field Parameters for p-Aminophenol

Serial Number	Description		Serial Number	Description	
1	101	0.2304	14	710	-0.0193
2	202	0.2304	15	809	-0.0700
3	102	-0.0478	16	812	0.0167
4	103	0.0000	17	811	-0.0048
5	104	0.0000	18	108	-0.1537
6	205	-0.0461	19	209	-0.1537
7	707	0.6309	20	310	-0.1707
8	808	0.4378	21	109	0.0271
9	1313	0.2000	22	608	0.0271
10	1414	0.2405	23	210	0.0541
11	1415	0.0000	24	211	0.0000
12	708	-0.1103	25	110	0.0000
13	709	0.0060			

Table (AP - X)

Non-planar Force Field Parameters Used in Calculating Fundamental Frequencies for 2,6:Dichloro p-Aminophenol

Parameter No.	Description		Parameter No.	Description	
1	101	0.2352	17	812	-0.0167
2	202	0.2352	18	809	-0.0700
3	303	0.2352	19	811	-0.0048
4	102	-0.0478	20	911	0.0167
5	103	0.0000	21	108	-0.1537
6	104	0.0000	22	209	-0.1537
7	205	0.0461	23	310	-0.1707
8	707	0.6310	24	109	0.0271
9	1010	0.6310	25	608	0.0271
10	808	0.4378	26	210	0.0560
11	909	0.4378	27	211	0.0000
12	708	-0.1103	28	110	0.0000
13	910	-0.1103	29	1313	0.4000
14	810	0.0061	30	1515	0.2500
15	709	0.0061	31	1314	0.0000
16	710	-0.0193	32	313	0.0000

Calculated Frequencies:*

Mode No.	Frequency (cm^{-1})		
1	1045	7	556
2	899	8	417
3	876	9	335
4	821	10	183
5	780	11	151
6	663	12	102

* See table (AP - XII) for the Cartesian displacements associated with these frequencies.

Table (AP- XI)

Non-planar Frequencies and Potential Energy Distribution for p-Aminophenol - Results obtained from trial force field of table (AP- IX).

		PED			
No.	Calculated Frequency	γ(N-H)	γ(O-H)	ϕ(C-C)	γ(C-O)
1	951	0.006	0.002	0.141	0.065
2	930	0.000	0.000	0.022	0.000
3	891	0.037	0.024	0.141	0.254
4	804	0.000	0.000	0.000	0.000
5	734	0.707	0.190	0.115	0.218
6	696	0.046	0.640	0.121	0.188
7	581	0.951	0.000	0.623	0.000
8	561	0.064	0.062	0.189	0.717
9	464	0.047	0.030	0.581	1.169
10	313	0.028	0.014	0.198	0.453
11	212	0.000	0.000	1.234	0.000
12	131	0.006	0.002	0.674	0.098

Table (AP-XII)

Cartesian Displacement Figures for 2,6:Dichloro p-aminophenol

	‡											
*	1	2	3	4	5	6	7	8	9	10	11	12
1	-0.005	0.002	0.000	0.000	-0.245	0.141	-0.085	0.000	0.041	0.000	0.006	-0.024
2	0.029	0.053	-0.056	0.000	0.149	-0.151	0.039	0.165	0.002	-0.013	0.006	0.006
3	-0.095	-0.159	0.149	0.000	-0.073	0.095	0.083	-0.097	-0.044	0.062	0.022	0.006
4	0.188	0.096	0.000	0.000	0.048	-0.091	-0.192	0.000	-0.019	0.000	0.024	-0.012
5	-0.095	-0.159	-0.149	0.000	-0.073	0.095	0.083	0.097	-0.044	-0.062	-0.007	0.006
6	0.029	0.053	0.056	0.000	0.149	-0.151	0.039	-0.165	0.052	0.013	0.024	-0.015
7	-0.001	-0.006	0.000	0.000	0.092	0.061	-0.008	0.000	-0.016	0.000	0.022	0.006
8	0.000	-0.001	0.001	0.000	-0.003	0.003	-0.002	-0.009	-0.005	-0.008	-0.010	-0.015
9	0.212	0.581	-0.645	0.000	-0.007	-0.092	0.166	-0.054	-0.002	0.012	-0.007	0.007
10	-0.163	0.062	0.000	0.000	0.005	-0.006	-0.009	0.000	0.011	0.000	-0.034	0.008
11	0.212	0.581	0.645	0.000	-0.007	-0.092	0.166	0.054	-0.002	-0.012	-0.019	-0.005
12	0.000	-0.001	-0.001	0.000	-0.003	-0.003	-0.002	0.009	-0.005	0.008	-0.634	0.008
13	0.622	-0.278	0.000	0.702	-0.026	0.048	0.143	0.000	0.059	0.000	-0.038	-0.005
14	0.622	-0.278	0.000	-0.702	-0.026	0.048	0.143	0.000	0.059	0.000	-0.038	-0.005
15	0.007	0.041	0.000	0.000	-0.698	-0.669	0.143	0.000	-0.116	0.000	-0.028	-0.021

* Atom number
‡ Vibrational mode

Chapter VI

The nuclear magnetic resonance spectra of the compounds considered in this study were recorded together with those of some of their derivatives. Table (NMR-III). The spectra of the benzene diazo-oxides are of particular interest since they seem to confirm the presence of a positive change on the (N_2) fragment. The spectrum of the parent compound has a multiplet structure which is typical of the unsymmetrically para- disubstituted benzene derivatives[56]. The four coupling constants which characterise this system were calculated using the models, AA'BB' and AA'XX'. The results of these calculations are summarised below.

The 2,6: and 2,5:dichloro derivatives give rise to simple nmr spectra having one and two signals respectively, the low field peak in the case of the 2,5:dichloro derivative is slightly broader than the high field one and this could be due to a certain degree of quadruple coupling between the positively changed nitrogen atom and the proton in the ortho position. The fact that no coupling is observed between the two protons is consistent with the observations and calculations carried out by Govil[16] on some quinone derivatives. The spectrum of the 2,3:dichloro parabenzene diazo-oxide consists of the expected quartet the analysis of which yields parameters which are somewhat similar to those found for the parent compound.

Calculation of Coupling Constants:

Para Benzenediazo-oxide:

The chemical shift difference between the centres of the two multiplets is approximately 91.2 Hz at least five times the expected value of the largest coupling constant JAX, (AB), nevertheless the spectrum is most probably of the AA'BB' type, figure (NMR-II).

Since each multiplet contains 12 rather than 10 lines which are expected in the AA'XX' case due to the degeneracy of transitions 1, 2 and 3, 4 [54, 56]. Let us assume for the time being that the molecule gives rise to an AA'BB' system then if we assign the most intense signals in the A spectrum at 50.37 and 40.53 Hz to the transitions ν_1 and ν_3 respectively we have since

$$N = \nu_1 - \nu_3$$
$$= 50.67 - 40.53 = 10.14 \text{ Hz}$$

The same value for N is obtained if AA'XX' behaviour is assumed and from the relationship[54]

$$((\nu_0 \delta) + N^2)^{\frac{1}{2}} = \nu_1 + \nu_3$$

where $\delta = \sigma_A - \sigma_B$

and using N = 10.14 we obtain

$$(\nu_0 \delta)^2 = 101.34 \times 81.06$$

$$\nu_0 \delta = 90.63$$

Now if the signals at 50.17 and 40.11 are assigned to the transitions ν_{11} and ν_9 respectively we obtain using

$$(M^2 + L^2)^{\frac{1}{2}} = \nu_9 - \nu_{11}$$

$$((M + \nu_o\delta)^2 + L^2)^{\frac{1}{2}} = \nu_9 + \nu_{11}$$

$$\therefore \quad M = 0.209, \text{ and } L = 10.06$$

The evaluation of K is not possible in a similar manner to that adopted in the cases of N, L and M, since no explicit algebraic expressions are available for the transitions involving K (JAA' + JBB'); in cases where AA' or BB' are para to one another K is put equal to M respectively since JAA' or JBB' would be very nearly zero: this is not the case in the system under consideration, and in order to obtain a value of K it is essential either to use the value from an AA'XX'analysis or solve the 4 x 4 submatrix for the energies of the basic product functions involved in the above mentioned transitions.

A computer programme was written which takes ν_A, ν_B, and the four coupling constants JAB - JBB' as input, generates the elements of the submatrix corresponding to functions (1So → 4So) reduces the latter to Hessenberg form and performs double Q.R. iteration to calculate to the eigen roots and eigen vectors of the submatrix.

The latter are normalised so that the largest element has the value unity. The process is repeated until "good" eigen values are obtained.

Thus using the set of parameters listed in Table NMR (I) the following transition energies may be calculated

a) $1s'o \rightarrow 1s'_1$ transition 2.

$$-(1s'o) + \frac{1}{2}(\nu A + \nu B) - \frac{1}{2}[(\nu\delta^2) + N^2]^{\frac{1}{2}} = E_2'$$

$$-(1s'o) - \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}} = E_2$$

where E_2 is now the transition energy relative to $(vA + vB)/2$

$(1s'o) = -90.4$ and $\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}} = 91.2$

$E_2 = 92.2 - 45.6$

$E_2 = 46.6$ Hz., obs. = 49.85 Hz.

b) $1s'{-1} \rightarrow 2s'o$ transition 4

$E_4 = (2s'o) + \tfrac{1}{2}(\nu_A + \nu_B) - \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$

$E_4 = (2s'o) - \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$

$E_4 = 85.9 - 45.6$

$E_4 = 40.3$ Hz; obs. = 40.8 Hz

c) $3s'o \rightarrow 2s'1$ transition 5

$E_5 = \tfrac{1}{2}\left[(\nu_o\delta)^2 - N^2\right]^{\frac{1}{2}} + \tfrac{1}{2}(\nu A + \nu B) - (3s'o)$

$E_5 = \tfrac{1}{2}\left[(\nu_o\delta)^2 - N^2\right]^{\frac{1}{2}} - (3s'o)$

$E_5 = 9.12 + 45.6$

$E_5 = 54.72$; obs. = 53.35 Hz

d) $2s'{-1} \rightarrow 4s'o$ transition 6

$E_6 = \tfrac{1}{2}(\nu A + \nu B) + \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}} + (4s'o)$

$E_6 = \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}} + (4s'o)$

$E_6 = 2.17 + 45.6$

$E_6 = 47.77$; obs. = 48.07 Hz

e) $4s'o \rightarrow 2s'1$ transition 7

$E_7 = \tfrac{1}{2}(\nu A + \nu B) - \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}} - (4s'o)$

$E_7 = E_7 - \tfrac{1}{2}(\nu A + \nu B)$

$E_7 = -2.17 + 45.6$

$E_7 = 43.43$; obs. = 42.53 Hz.

f) $2s'_{-1} \rightarrow 3s'_o$ transition 8

$$E_8 = (3s'_o) + \tfrac{1}{2}(\nu A + \nu B) + \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$$

$$E_8 = (3s'_o) + \tfrac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$$

$$E_8 = 45.6 - 9.12$$

$E_8 = 36.48$; obs. = 37.25 Hz

However from the values of L and N calculated above and since we have,

$K = JAA' + JBB'$ $N = JAB + JAB'$

$M = JAA' - JBB'$ $L = JAB - JAB'$

$JAB = \frac{1}{2}\,(10.14 + 10.06) = 10.1$ Hz

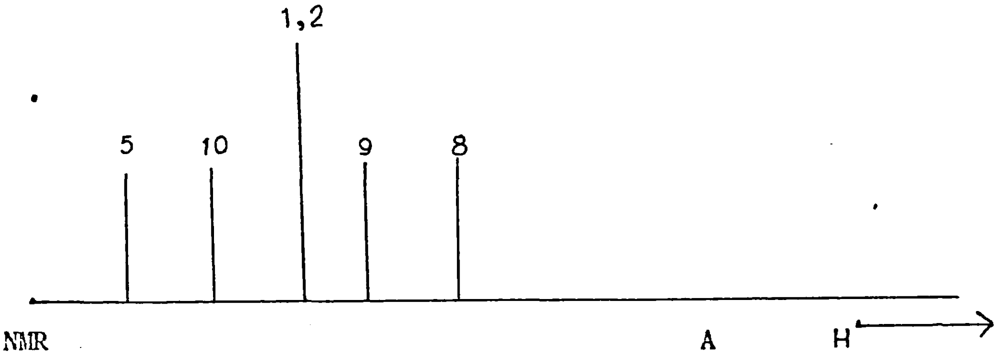
$JAB' = \frac{1}{2}\,(0.08) = 0.04$ Hz

Let the protons in this molecule constitute an AA'XX' system, then four distinct coupling constants are required, namely

JAX, JAX', JAA' and JXX'

and the spectrum should be symmetric about ($\nu A + \nu B$)/2 each half containing 10 lines wich are again symmetric about their respective values.

The A-part of the spectrum would have the general shape:



Now transitions 1 and 3 are quite readily assigned to the most intense signals at 5.07 and -5.07 Hz.- measured relative to $\delta\nu_A$ - but since

$$N = \nu_1 - \nu_3 \; ; \quad JAX + JAX' = 10.14$$

and if furthermore we assigned the signals at 8.35 and 3.07 Hz to transitions ν_5 and ν_6 we have.

$$K = \nu_5 - \nu_6 = 5.28$$

and $L_2 = (\nu_5 + \nu_6)^2 - K^2$

$$L = 10.12$$

K is given by K = JAA' + JXX'

and L = JAX - JAX'

Now in order to arrive at a value for M it is necessary to assign at least one more transition e.g. ν_9 or ν_{12}, if ν_9 is assigned to the signal 4.57 we obtain

$$2 \times 4.57 = M + (M^2 + L^2)^{\frac{1}{2}}$$

$$L = 10.12$$

$$M = \frac{L^2 - 9.14^2}{18.28} = 1.06$$

and since M is given by

$$M = JAA' - JXX'$$

we can now calculate:

$$JAX = 10.13 \text{ Hz}$$

$$JAX' = 0.01 \text{ Hz}$$

$$JAA' = 3.17 \text{ Hz}$$

$$JXX' = 2.11 \text{ Hz}$$

The coupling constants compare rather well with the "average" values for aromatic rings[55].

$J_o = 8$ Hz ($\equiv$ JAX); $J_m = 2$ Hz; ($\equiv$ JAA'); $J_p = 0.5$ Hz ($\equiv$ JAX')

Table (NMR-I)

Calculated Parameters Using Method I

$\nu o \delta$	91.0
JAB	9.0
JAB'	0.05
JAA'	3.00
JBB'	4.00

Table (NMR-II)

Calculated Transition Frequencies Using Method I

Transition No.	Calc. Hz*	Obs. Hz*
1 s'o 1s'$_1$ 2	46.6	49.85
1s'-1 2s'o 4	40.3	40.80
3s'o 2s'$_1$ 5	54.72	53.35
2s'-1 4s'o 6	47.77	48.07
4s'o 2s'$_1$ 7	43.43	42.53
2s'-1 3s'o 8	36.48	37.25

* Relative to $(\nu A + \nu B)/2$

Table (NMR-III)

The NMR spectra of some of the compounds considered in this study

Compound	Frequency	(Hz)	Type	Solv.	Ref.
Para Benzene Diazo-oxide	375	466	M	$CDCl_3$	TMS
2,3:dichloro p-benzene diazo-oxide	388	426*	Q	$CDCl_3$	TMS
2,5:dichloro p-benzene diazo-oxide	389	486	D	$CDCl_3$	TMS
2,6:dichloro p-benzene diazo-oxide	343		S	$CDCl_3$	TMS
2,3:dichloro p-benzoquinone	420		S	$CDCl_3$	TMS
2,5:dichloro p-benzoquinone	430		S	$CDCl_3$	TMS
2,6:dichloro p-benzoquinone	425		S	$CDCl_3$	TMS
2,3: dichloro p-hydroquinone	429		S	DMSO	TPS
2,5:dichloro p-hydroquinone	432		S	DMSO	DMSO
2,6:dichloro p-hydroquinone	425		S	DMSO	DMSO

* Spectrum obtained using Varians (HA-100) instrument.

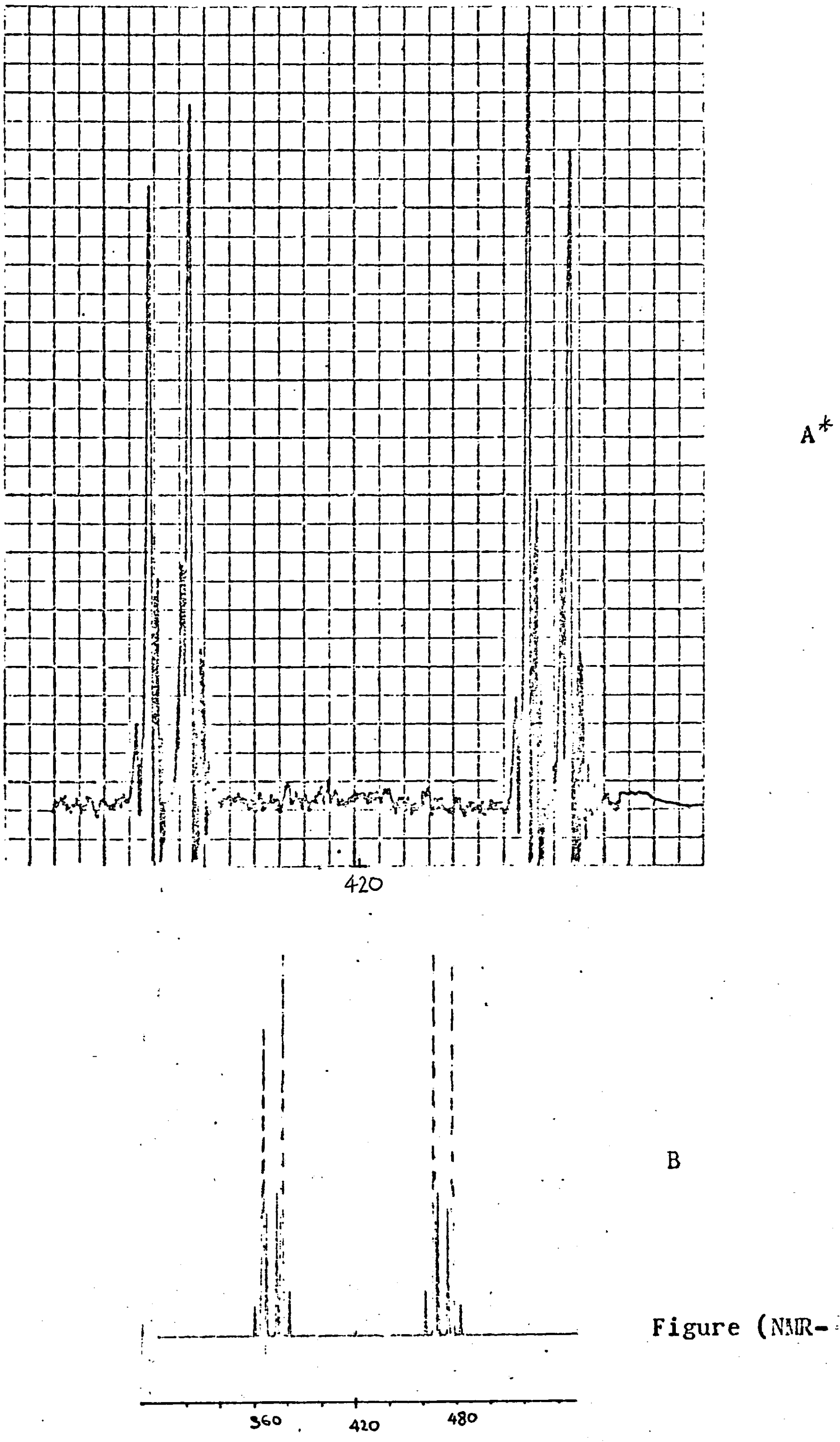


Figure (NMR-II)

Observed (A) and calculated (B) NMR spectra of 1,4:Benzene diazo-oxide

* 2.5 cm ≡ 42 Hz

Chapter VII

The Normal Co-ordinate Analysis

The calculation of the vibrational frequencies, Cartesian displacements, potential energy distribution and other related quantities, was used in this study firstly as a guide to the assignments of the fundamental vibrations, and secondly in order to obtain "improved" force field parameters for some of the molecules studied here, notably for parabenzoquinone and some of its chloro derivatives. In the first case reliance is made upon the assumption that, with the use of the "appropriate" force constants and a reasonable geometrical model one should be able to obtain some idea about the dynamics of the molecule under consideration. It is obvious from the outset that the information obtained from such calculations, should be treated with a good deal of caution, since although the equilibrium molecular dimensions might be readily accessible one is never certain how much will the choice of a given force constant or set of force constants alter the results of the calculation. The use of other criteria in making a given assignment should, however, insure that the dangers which might be caused by a misguided choice of a set of force field parameters are kept at a minimum.

The calculation of improved force field parameters for parabenzoquinone and some of the other molecules considered here, has been carried out for two main reasons, the first being to assist in the assignments of the spectra of the diazo-oxides and secondly in order to gain some insight into the dynamics of the parabenzoquinone molecule and study the differences between the quinonoid and benzenoid force fields. Emphasis in the refinement work was laid upon the non-planar vibrations of the quinones primarily because they constitute a smaller problem than the planar ones; and, therefore, involve a smaller set of force field parameters than the planar problem.

The problems involved in the refinement of potential energy parameters are very considerable, and some of the difficulties encountered in such calculations have been mentioned by a number of workers[44, 45, 47]. Briefly it may be said, that provided the assignments of the fundamental vibrations are correct and that the number of the experimental points, or frequencies, is greater or at least equal to the number of force field parameters, then one can hope to obtain a sensible set of refined force field parameters by applying one of the standard refinement techniques.

In the least squares method which is used in this work, the efficiency of a refinement cycle is determined by the condition of the matrix $(J'PJ)$ whose inverse is to be calculated in each cycle. Clearly the smaller this matrix i.e. the smaller the number, r, of parameters to be refined in a given cycle - the greater is the chance that the matrix will be non-singular, and hence the solutions Δf_i well determined. So that if we have, r, parameters to refine where r is greater than the number of experimental frequencies then we must either find a set of relationships between these parameters which enables us to reduce the effective number of parameters. Alternatively one could refine a certain fraction of the force field in every cycle. Both methods have been tried in this work; in the case of the planar parabenzoquinone problem.

The first although yielding well-conditioned matrices was found to slow down convergence considerably and did not always yield sensible values of the force constants owing to the essentially arbitrary nature of the assumptions involved in setting up the relationships between the various force constants of the valence force field. The second method was found more satisfactory firstly because it does not involve inter-relating the force field parameters in any way and furthermore it does not hamper the convergence. An objection that might be raised against this method is that "over-correction" of a set of force constants during a cycle of refinement might produce erroneous corrections Δf_i for the set of parameters in the next refinement cycle. This is avoided in the present work by dividing the error vector $\Delta \lambda$ by a factor, $d > 1$, this has the effect of scaling down the corrections Δf_i and slowing down the convergence slightly but appears to eliminate the dangers of "over-correcting" a set of parameters.

This is readily demonstrable by carrying out the refinement of different sets of force constants in a different order in two or more runs, whence it may be seen that the final force fields are the same in each case at least to the third decimal point. Since $\Delta\lambda_i$ are largest at the start of the refinement process it is advisable to decrease d as the refinement proceeds. Thus in a characteristic refinement process where the average $\Sigma\nu_i/\nu_i$ might be as high as 60 cm^{-1}; d is put equal to , say, 40 at the beginning of the refinement and allowed to decrease to 1-5 as convergence is approached.

In the refinement work carried out here corrections to the largest possible number of parameters are calculated at every cycle of the refinement; this amounts to between 12 and 15 force constants depending upon the type of constants being improved.

The Diazo-oxides and Quinones:

Comparison of the spectra of similarly substituted diazo-oxides, quinones and benzene derivatives may be shown to support a quinonoidal structure for the diazo-oxides it is, nevertheless, apparent that certain important differences exist between the spectra of the diazo-oxides and the corresponding quinones. These differences are possibly largely due to the important contribution made by the phenoxide-type structure which involves a fully aromatic nucleus in the case of the diazo-oxides. Thus the ν(C-O) stretching mode gives rise to a strong absorption in the spectra of the diazo-oxides which, however, occurs at a much lower frequency than the corresponding quinone absorption. Furthermore the highest ν(C-C) stretching vibration in the spectra of the diazo-oxides appears to be considerably weaker than its counterpart in the quinone spectra. The spectra of 2,6:dichloro p-benzenediazo-oxide, for instance, may infact be seen to represent an intermediate stage between the spectra of the diazonium hydrochloride and the corresponding quinone, in terms of the intensities of the ν(C-C) stretching vibrations and the position of the ν(C-O) stretching absorption.

Chlorine substitution at the diazo-oxide ring does not appear to influence the intensity or the position of the ν(C-O) stretching absorption. The ν(N-N) stretching vibration is, however. affected by the substitution pattern since it occurs around 2180 cm^{-1} in the spectrum of 2,3:dichloro p-benzenediazo-oxide, and in the region 2100-2120 cm^{-1} in the case of the remaining diazo-oxides, table (DO-X). This may be attributed to the influence of steric factors in the case of the 2,3:dichloro derivative, since the two chlorine atoms in an ortho-position with respect to one another would tend to force the (C-N-N) group into a position in which π-bonding interactions with the ring become difficult and the triple bond character of the (N-N) bond is thus enhanced. The difference in the position of the (N-N) stretching vibrations in the parent compound, on the one hand, and in the 2:chloro or the 2,6:dichloro p-benzenediazo-oxide, on the other, is rather small - 10 cm^{-1}. It may nevertheless be suggested that chlorine substitution in these positions increases the triple bond charecter of the (N-N) link, possibly by making it more difficult for the oxygen atom to feed some of its negative charge back into the ring system, thus decreasing the importance of the quinonoidal form as a contribution to the overall structure of the diazo-oxide molecule.

The Cartesian displacements calculated for parabenzoquinone's planar vibrations resemble those found for paradichlorobenzene[39]. The main difference being due to the fact that the (C-X) stretching vibration, naturally, appears to contribute to the higher frequency modes in the various symmetry classes in the case of parabenzoquinone. In addition to this, it appears that the (C-H) bending charecter is less radily associated with particular group frequencies, since the (C-Cl) stretching and (C-H) bending vibrations appear to be rather delocalised.

The reasons for this ill-behaviour, if it may be described as such, are thought to be, firstly, the reduced symmetry of the diazo-oxides and their chloro derivatives and, secondly, the uncertainty about the non-diagonal force constants, in particular. In this connection, it is perhaps significant that the calculated non-planar vibrations of quinones and the diazo-oxides are, in general, much "better behaved" than the planar ones.

The Aminophenols and Hydroquinones:

The vibrational spectra of these compounds have the following points in common; both types of molecules have skeletal modes of vibration coupled more or less strongly to the (X-H) vibrations and both insufficiently soluble in suitable spectroscopic solvents, both of these charecteristics render a comparative study of their spectra with those of the quinones and diazo-oxides , considered here, somewhat more complicated. It is, nevertheless, readily noticeable that the spectra of the aminophenols and hydroquinones having the same substitution patterns are quite similar, and that they possess a number of important differences from the spectra of the quinones and diazo-oxides. The similarities between the spectra of the aminophenols and hydroquinones are quite apparent in the case of the out-of-plane (C-H) deformation, and some of the (C-Cl) stretching vibrations. Such similarities are also apparent in the higher (C-C) stretching region where the positions, the intensities and band shapes of the ν(C-C) absorptions may be seen to be in close resemblance in the respective spectra. One notable exception in the infrared spectrum of 2,6:dichloro p-hydroquinone is the highest (C-C) stretching absorption which resembles very closely that observed in the spectrum of 2,6:dichloro p-aminophenol hydrochloride rather than the aminophenol itself, being of a higher intensity than that observed in the spectra of the remaining hydroquinones and aminophenols. This absorption which occurs around 1600 cm^{-1} is also seen to have a much weaker intensity in these compounds than that observed in other para-substituted benzene derivatives. The remaining (C-C) stretching absorptions show signs of being very much influenced by the (X-H) vibrations.

Another point which emerges from comparative examination of the spectra of the aminophenols and hydroquinones is the assignment of the (O-H) - in-plane - bending mode to the broad and moderately intense band occuring in the region 1300 - 1370 cm^{-1} in their spectra. This absorption as well as a similarly intense and extremely broad band around 900 cm^{-1} - assigned as the γ(N-H) mode - are characteristic of the aminophenol spectra considered in this study.

Another non-planar (N-H) deformation appears to occur around 1100 cm^{-1}. Both assignments appear to derive a certain amount of support from the calculated frequencies as well as deuteration experiments. The diagonal γ(X-H) constants are in the region of 0.3×10^{-11} erg rad^{-2}. It was found that the use of diagonal constants which depart substantially from this value produces anomalous values for the (C-C) torsion frequencies, this is almost certainly due to the fact that the non-diagonal force constants involving (X-H) deformations have been ignored in these calculations.

Chapter VIII

Experimental:

Preparation of the hydroquinones:

Hydroquinone (HQ): itself was obtained commercially and purified by recrystallisation from chloroform.

2:Chloro p-hydroquinone (2HQ): was prepared by passing HCl gas through a chloroformic solution of p-benzoquinone until a weight increase of about 30% was obtained.[52] The product was filtered, dried and recrystallised several times from carbon tetrachloride.

2,3:Dichloro p-hydroquinone (23HQ): was obtained in 30% yield by passing chlorine gas through a glacial acetic acid solution of p-hydroquinone at 50°C; until a weight increase of about 33% was obtained. The crystalline paste obtained from the concentrated solution was filtered, dissolved in water and filtered hot, the filterate was boiled with charcoal and left to cool, and the white crystals which separated were recrystallised from chloroform.

2,5: and 2,6:Dichloro p-hydroquinone (25,26HQ): were prepared from their respective quinones by reduction with sodium dithionite in an aqueous alcoholic solution which was maintained at 50 to 60°C on a water bath. The white needles which separate on cooling were purified by recrystallisation from chloroform.

Preparation of the Quinones:

All except 2: and 2,3:Chloro p-benzoquinones were obtained commercially, and both of these were prepared from their hydroquinones.[50] 1 Mol. of hydroquinone, 0.5 mol, of sodium chlorate and about 0.5g of vanadium pentoxide were added to 1 litre of 2% sulphuric acid. The mixture was stirred for 4 to 6 hours at 0-10°C and the yellow solid which formed was washed with cold water and dried over calcium chloride. The pure quinones were obtained by recrystallisation from petroleum ether (60-80°C).

Preparation of the p-Benzenediazo-oxides

The diazo-oxides were all prepared from their corresponding hydrochlorides by treatment, in absolute alcohol, with freshly prepared silver oxide[9]. The diazonium salts were prepared from the aminophenol hydrochlorides by adding amyl nitrite (1.2 mol.) to a suspension of the hydrochloride in 20 ml. of conc. ethanolic HCl. The salt was precipitated using 300 ml. of sodium dried ether.

Preparation of the Aminophenol Hydrochlorides:

Para-aminophenol hydrochloride was prepared from commercially available p-aminophenol, by passing HCl gas through an ethereal solution of the amine. The hydrochloride was purified at least three times by dissolving in methanolic HCl and reprecipitating with ether.

2:Chloro p-aminophenol Hydrochloride was prepared from 2:Chloro p-nitrophenol.

The 2:Chloro p-nitrophenol was prepared by heating a mixture of 10g of p-nitrophenol with 200 ml. conc. HCl in a beaker until solution was complete. The solution was stirred and cooled to room temperature. 3g. of potassium chlorate in 60 ml. of water was added gradually from a separating funnel, which had its stem immersed in the mixture, while stirring was continued vigorously.

The mixture which became a thick paste towards the end of the reaction was allowed to stand for a few hours. After filteration, washing with water and drying, 11g of nearly white 2:Chloro p-nitrophenol was isolated and purified by recrystallisation from an acetic acid/water mixture(m.p. of pure solid 110°C). Reduction of 2:Chloro p-nitrophenol was accomplished by gradually adding sodium dithionite (40g) to 10g of 2:Chloro p-nitrophenol in 60 ml. of boiling water containing 0.27g of sodium hydroxide until the colour disappeared. The solution was filtered and allowed to cool to room temperature, whereupon long needles of 2:Chloro p-aminophenol were formed. After filteration, washing with water and drying the aminophenol was recrystallised from hot water. The hydrochloride was obtained by passing HCl gas through an ethereal solution of the aminophenol.

<u>3:Chloro p-aminophenol Hydrochloride</u>

10g of (NO)diacetyl p-aminophenol were dissolved in 100ml. of glacial acetic acid and dry chlorine gas passed through the solution until a weight increase of about 3.5g was obtained, the solution was then concentrated to half of its original volume, by evaporation under reduced pressure, and 10ml. of water were added and the mixture cooled in ice. The white needles which separated after a few minutes were filtered off, washed with water and dried before being recrystallised from an acetic acid water mixture (m.p. of pure compound 130°C yield:

70%).

3:Chloro p-aminophenol:HCl was obtained from the diacetyl derivative by refluxing with a few ml. of conc. HCl.

This preparation of 3:Chloro p-aminophenol hydrochloride does not appear to have been reported in the literature.

2,5:Dichloro p-aminophenol hydrochloride:

36 g of p-phenacetin were dissolved in 200 ml. of glacial acetic acid and 17 g of sodium chlorate in a little water added to the solution, this was followed by 60 ml. of conc. HCl; the mixture was shaken and allowed to stand for 15 minutes before 300 ml. of water were added. The pinkish-white solid which separated immediately was filtered, washed with water and recrystallised several times from an alcohol-water mixture. The yield of the pure product was rather poor: 35% m.p. 162°C.

A higher yield was obtained from direct chlorination of phencetin in glacial acetic acid (50% m.p. 162°C).

2:Cloro p-phenacetin is formed in 25% yield together with some tetrachloro p-phenacetin.

10g of 2,5:Dichloro p-phenacetin were refluxed for ten hours with 15 ml. of constant boiling hydriodic acid. On cooling the reaction mixture a cream coloured solid was obtained, this was filtered, washed with conc. HCl and dried. By refluxing the hydriodide with conc. HCl the hydrochloride was obtained. This was purified by repeatedly dissolving in methanolic HCl and reprecipitating with ether. (yield = 47%).

2,6:Dichloro p-aminophenol Hydrochloride was prepared from 2,6:Dichloro p-nitrophenol by reduction with sodium dithionite. The 2,6:Dichloro p-nitrophenol was prepared by passing chlorine gas into a solution of 10g of p-nitrophenol in 65 ml. of acetic acid, and the gas was passed through until a weight increase of 5g was obtained. The solution was concentrated by heating on a water bath under reduced pressure and the solid which separated upon cooling to room temperature was filtered washed with water and allowed to dry. (yield 90%).

2,3:Dichloro p-aminophenol Hydrochloride was prepared from 2,3:Dichloro p-nitrophenetol by reduction with tin metal and conc. HCl at 70°C in 60% yield. The amine thus obtained (an oil, m.p. 2°C b.p. 125°C 8 cm.) was purified by steam distillation and then converted into the acetyl derivative from which 2,3:Dichloro p-aminophenol hydroiodide was obtained by treatment with constant boiling hydroiodic acid under reflux.

The hydrochloride was obtained by refluxing with conc. HCl for 30 minutes, the product was filtered off and purified as described above.

Deuteration Experiments:

Deuteration of the OH and NH_2 groups in the hydroquinones and aminophenols considered here was carried out by repeatedly dissolving about 2.0g of the compound in D_2O at slightly elevated temperatures and precipitating by cooling at 0°C filtering off in a dry box and drying over calcium chloride under reduced pressure before the operation was repeated. It was found that 2-4 cycles produced deuterated species in which the intensity of the (C-H) stretching absorption was reduced to about one tenth of its original value, in 50-60% yield.

The infrared spectra of the compounds included in this study were recorded as solutions and mulls on a Beckman IR-9 double beam spectrophotometer which uses KBr optics and is capable of a resolution of about 1 cm^{-1}. The experimental frequencies are all accurate to 1 cm^{-1} except where otherwise indicated. All spectra were recorded under medium and low gain conditions, at 8 cm^{-1} min^{-1}.

The spectra of deuterated p-hydroquinone and p-aminophenol were recorded using a Perkin-Elmer 225 spectrophotometer which uses CsI optics and has comparable resolution and accuracy to the above mentioned instrument.

The far infrared spectra were recorded on RIIC's interferometer FS (720) and the results obtained from these measurements are accurate to 2 cm^{-1}. The samples used were polythene and wax discs.

The Raman spectra were measured using Imperial College's Laser Raman instrument.

A Spex Raman instrument using an Argon/Krypton Laser was also used to record the spectra of the quinones, and a Carey Instrument which uses a Helium/Neon Laser was used for recording the spectra of some of the hydroquinones.

Spectroscopic grade solvents were used in the solution studies without a compensating cell in the reference beam. The solid phase spectra were recorded using Nujol, Flurobe and Kel-F mulls.

Nuclear Magnetic Resonance Spectra:

The nmr spectra reported in this work were recorded on a Varian HA 60 IL instrument. Solvents used were deuterochloroform and carbon tetrachloride. TMS and TPS were used as internal standards.

Melting points of the Quinones

	2Q	23Q	25Q	26Q	2356Q
M.P.	56.5	96.5	162	120	293
Lit. M.P.	57.0	96.0	161-2	121	292
Yield (%)	65	58	-	-	-

Melting points of the Hydroquinones

	HQ	2HQ	23HQ	25HQ	26HQ	2356HQ
M.P.	171	106	145	170	163-4	
Lit. M.P.	170.5	106	144	170	164	
Yield	-	57	53	51	63	
Diacetyl Derivative (M.P.)	-	99	121	141	111	

Melting points of the Diazo-oxides

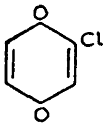
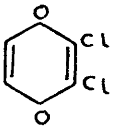
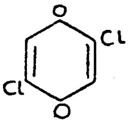
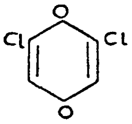
	DO	3DO	23DO	25DO	26DO
M.P.	39/99 Anh.	112	125	140	162
Lit. M.P.	39/96 Anh.	-	-	-	-
Yield (%)	10	23	5	17	45

Melting points of the Aminophenol

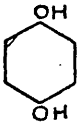
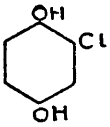
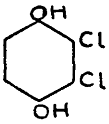
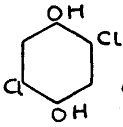
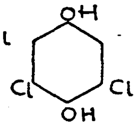
	AP	2AP	3AP	25AP	26AP	2356AP
M.P.	184	152	160	158*	165-6	210
Lit. M.P.	184	153	160	-	166	-
Yield	-	61	37	41	65	62

B:HCl

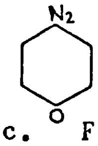
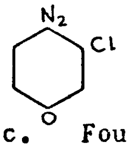
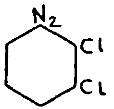
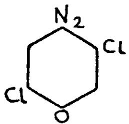
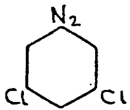
Analyses of the Quinones

						
	Calc.	Found	Calc.	Found	Found	Found
C	55.2	55.4	40.6	40.9	41.2	42.1
H	2.1	2.0	1.1	1.5	1.4	1.6
O	22.4	21.3	19.2	18.8	17.9	18.2
Cl	24.9	23.9	40.1	39.8	40.5	40.2

Analyses of the Hydroquinones

								
	Calc.	Found	Calc.	Found	Calc.	Found	Found	Found
C	65.4	66.7	49.8	51.3	40.2	40.9	41.2	40.8
H	5.4	5.8	3.4	3.1	2.2	2.5	2.4	2.6
O	29.9	27.5	22.9	21.8	17.8	17.2	16.8	16.7
Cl			24.5	23.8	39.5	39.1	39.3	39.6

Analyses of the Diazo-oxides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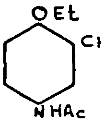
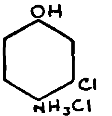
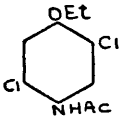
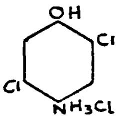
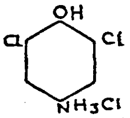
H	3.4	3.4	1.9	2.0	1.06	1.3	1.6	1.4
N	23.3	22.7	18.1	17.9	1.48	14.8	14.8	14.9
O	13.4	12.9	10.0	9.9	8.4	8.5	7.9	7.7
Cl			22.9	23.1	37.4	37.2	37.8	37.8

Analyses of the Aminophenol derivatives

									
Element	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Found
C	56.2	56.5	40.0	40.3	48.3	50.4	33.6	34.2	34.4
H	5.6	5.9	3.8	4.3	48.4	48.8	2.8	3.1	2.6
N	6.5	6.7	7.7	7.6	5.6	5.3	6.5	6.2	5.9
O	14.9	14.5	8.8	8.2	15.3	12.2	7.5	8.1	7.7
Cl	16.6	16.4	39.4	39.7	28.6	27.3	49.5	48.4	49.4

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Appendix I.

Listings of some of the programmes used in this work are given below. These programmes were initially written in EXCHLF for London University's Atlas computer, but have since been translated into FORTRAN in view of the imminent scrapping of the former computer. All the programmes given below have been streamlined in order to save time and core store and have also been fully tested in conjunction with their EXCHLF counterparts.

A - Master INPLANE: This programme takes as input data the X- and Y- co-ordinates of the atoms in the nucleus as well as the bond lengths and bond angles (A), and (U) respectively; it then reads the corresponding parameters involving the substituents. It calculates the G-matrix and the W-matrix (B701) using the reciprocal co-efficients of the internal reciprocal coefficients of the internal co-ordinates which are provided as input data (IZ). In order to test the calculation the G-matrix is solved and its eigen-values output for inspection. A trial force field may also be input and the planar frequencies may thus be determined.

B - Master BEDVIB: The programme uses the bond lengths (A) and bond angles (U) to calculate the W-matrix for the non-planar vibrations os a benzene type molecule, and determines the non-planar frequencies using a trial force field, whose elements (ZPOT) are distributed in the F-matrix in the manner indicated by the integer arrays (IZ). These specify the row and column labels in the potential energy matrix which are allocated to a given force constant. In this programme (NNKL) is the number of molecules to be treated, (N) is the number of atoms in any one of these molecules, and (ISYM) is the number of symmetry classes in each molecule.

C- Master BEDCOMII: This is one of the force constant refinement programmes used in this work.

Input Data

1. The first card contains the following information;

    a) the dimension of the problem including the redundant coordinates, (N),

    b) the number of symmetry classes into which the symmetric secular matrix is factorised, (IH49),

    c) a factor to be used in scaling the error vector, (IDIV),

    d) three parameters (ICAR), (IREF) and (MARY) which indicate whether refinement, Cartesian displacements and Cartesian displacement plots are required.

2. The W-matrix (B701) to be used in generating the symmetric secular matrix; this normally requires more than one card.

3. The sizes of the factors in the secular matrix.

4. This card should contain two numbers;

    a) one to determine whether the improved force field parameters obtained in a given cycle are to be used in the next cycle (IC31=4049) or not (IC31= any other five digit number),

    b) the total number of parameters used in the force field to be tried (IRE).

5. The force field parameters (XINIT).

6. Non-zero elements of a matrix (IZ) which specify how the elements of (XINIT) are to be located in the potential energy matrix. Thus suppose that the force constant f_{ij} involves a particular type of interaction between members of two sets of internal co-ordinates then two separate sets of data should be provided: a) the number of times this particular cross term occurs in the potential energy matrix, b) the numbers of the interacting co-ordinates, arranged in pairs with a minus sign preceeding the first number if the particular interaction has the opposite sign to that indicated by the force constant - in the array (XINIT).

7. The observed frequencies (IOBS).

8. The remaining data concern the details of how the refinement process is to be conducted and the necessary data for calculating the CDF if required:

a) the number of refinement cycles (IK) is given first,

b) the number of parameters to be improved in the i^{th} cycle (ICOT), and the required number of iterations in the cycle (ISS),

c) the serial number of the parameters to be improved. This part of the program may be readily modified to accept the serial numbers of a set of parameters together with suggested values for trial where the latter figure may be different from that given in (XINIT). This modification is particularly useful when no refinement is required, i.e. IREF≠0.

d) The matrix to be provided for calculating the Cartesian displacements is required only if ICAR=0; both this matrix and the W-matrix are produced by the segments INPLANE and BEDVIB, described above.

Output Data

The programme outputs a history of the refinement cycles followed by a summary of the process and the best set of parameters at each point, together with the potential energy distribution figures, the weighted sum of the squares of the differences between the observed and calculated frequencies, the variances and the correlation matrix.

The subroutine required for producing Cartesian displacement plots from the Cartesian displacement figures - MARI - has not been included since it will depend upon the graph plotter package in use in any computer centre.

The programme OFBQ091 is essentially a modified version of BEDCOMII which can handle up to five molecules in a refinement attempt. In this program ISO=ISYM=5, and B701, B702,...B705 are the W-matrices of the molecules in question and the arrays IH1, IH2,...IH5 contain the orders of the symmetry classes of the secular matrices.

The combination bands reported in this work were calculated using a programme which takes as input the wavenumbers of the fundamental vibrations and the possible combinations, computes all possible binary and ternary combinations and outputs the results after testing their compliance with preset tolerance conditions.

(BEDVIB)

```
      DIMENSION A(12,12),U(12,12),Z(144),BB(144),WORK(144),WOR1(144),F(1
     144),G(144),FSYM(144),GSYM(144),TRAZ(144),TRAW(144),TRAE(144),E(144
     1),AMAS(144),XPOT(22),YPOT(30),ZPOT(30),WOR2(144),B701(144),B801(14
     14),ID(30),IZ(300),CAPP(2),GA(20),GB(20),GC(20),GE(20),IX(10)
   10 FORMAT(I4)
   20 FORMAT(6F10.6)
   60 FORMAT(8F10.4)
   80 FORMAT(6F8.4)
   90 FORMAT(2I5)
  100 FORMAT(16I5)
  190 FORMAT(I5)
  200 FORMAT(///(12F8.4))
  350 FORMAT(1H1,(///(12F8.4)))
  400 FORMAT(8F8.4)
  500 FORMAT(4I5)
  600 FORMAT(F10.4)
 2000 FORMAT(1H1,/25H G-MATRIX****************)
 2010 FORMAT(1H1,/25H SYM G-MATRIXTRIX********)
 2030 FORMAT(1H1,/25H DIAGONAL G-MATRIX*******)
 2040 FORMAT(1H1,/25H DIAGONAL SEC. EQN.******)
 2050 FORMAT(1H1,/25H EIGEN-FREQUENCIES.******)
 2100 FORMAT(1H1,/25H B701**W-MTRIX***********)
 2200 FORMAT(1H1,/25H CART DISP MATRIX********)
 1000 FORMAT(I5,I3,F12.4)
 1010 FORMAT(I5,I3,F12.2)
 1020 FORMAT(I5,F12.4)
 1030 FORMAT(22H DIMENSIONS AND MASSES)
 1060 FORMAT(2I5,2A8)
 1090 FORMAT(2A8)
      KKKN=0
C READ NUMBER OF MOLECULES TO BE TREATED
      READ(1,190) NNKL
 8800 KKKN=KKKN+1
C READ NUMBER OF ATOMS (N) IN MOLECULE (I) AND THE NUMBER OF SYMMETRY CL SSES
C ISYM THEN  READ 16 CHARECTER COMMENT
      READ(1,1060)N,ISYM,CAPP(1),CAPP(2)
      WRITE(2,1090) CAPP(1),CAPP(2)
      L=0
      O=1
      M=L
```

```
      ME=N+1
      API=3.1415926/180.0
      M2=2*M
      IF(KKKN-1) 55,56,55
C READ BOND LENGTHS AND BOND ANGLES STARTING FROM 106 IN C. W. DIRECTION
   56 READ(1,20)(GA(I),I=1,M2)
   55 KI=1
      I=1
      J=L
      DO 1,K=1,M
      A(I,J)=GA(KI)
      U(I,J)=GA(KI+1)
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      A(J,I)=A(I,J)
      I=I+1
      J=I-1
      KI=KI+2
    1 CONTINUE
      J=L
      I=1
      DO 2,K=1,M
      II=I+1
      NI=N*(I-1)+J
      Z(NI)=-1/(A(I,J)*SIN(U(I,J)))
      I=I+1
      J=I-1
    2 CONTINUE
      I=1
      J=L
      JE=J
      DO 3,K=1,M
      II=I+1
      IF(I-M)27,26,27
   27 NI=N*(I-1)+I
      Z(NI)=(A(I,II)-A(I,J)*COS(U(I,J)))/(A(I,II)*A(I,J)*SIN(U(I,J)))
      Z(NI)=Z(NI)-(COS(U(I,II))/(A(I,II)*SIN(U(I,II))))
      I=I+1
      J=I-1
    3 CONTINUE
      GO TO 28
```

```
   26 II=1
      GUTO 27
   28 I=1
      J=L
      DO 4,K=1,M
      IP=I+1
      IPP=IP+1
      II=I+1
      IF(IP-M)30,37,38
   30 NI=N*(I-1)+II
      Z(NI)=(A(I,II)-A(IP,IPP)*COS(U(I,II)))/(A(I,II)*A(IP,IPP)*SIN(U(I,
     1II)))
      Z(NI)=-Z(NI)+(COS(U(I,J))/(A(I,II)*SIN(U(I,J))))
      I=I+1
      J=I-1
    4 CONTINUE
      GO TO 39
   37 IPP=1
      GO TO 36
   38 IP=1
      IPP=2
      II=1
      GO TO 36
   39 I=1
      J=I+2
      DO 5,K=1,M
      IN=I
      IP=I+1
      JJ=J-1
      IF(IP-M)29,25,24
   29 NI=N*(I-1)+J
      Z(NI)=1/(A(IP,J)*SIN(U(IN,JJ)))
      I=I+1
      J=I+2
    5 CONTINUE
      GO TO 45
   24 J=2
      IP=1
      IN=1
```

```
      JJ=L
      GO TO 29
   25 J=1
      IP=I+1
      J=1
      GO TO 29
   45 LL=L+1
C READ BOND LENGTHS INVOLVING SUBSTITUENTS FROM 107-612.
   50 READ(1,20)(GB(I),I=1,M)
   51 KKK=1
      DO 6 K=LL,N
      I=N*(K-1)+K
      A(K,K)=GB(KKK)
      KKK=KKK+1
      Z(I)=1/A(K,K)
    6 CONTINUE
      IF(KKKN-1) 91,92,91
C READ BOND ANGLES INVOLVING SUBTS. STARTING 607,107,.... ETC.
   92 READ(1,20)(GC(I),I=1,N2)
   91 I=L+1
      J=L
      IK=1
      DO 7 K=1,L
      U(I,J)=GC(IK)
      IK=IK+1
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      J=I-L
      I=I+1
    7 CONTINUE
      I=L+1
      J=1
```

```
      DO 8 K=1,L
      U(I,J)=GC(IK)
      IK=IK+1
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      I=I+1
      J=J+1
    8 CONTINUE
      I=L+1
      J=L
      DO 9,K=1,L
```

```
      IQ=I-L
      NI=N*(I-1)+J
      Z(NI)=(SIN(U(I,J)))/(A(IQ,J)*SIN(U(IQ,J)))
      I=I+1
      J=IQ
    9 CONTINUE
      II=L
      I=L+1
      J=2
      DO 11,K=1,L
      JJ=J-1
      IF(J-L)46,46,47
   46 NI=N*(I-1)+J
      IQ=I-L
      Z(NI)=(SIN(U(I,JJ)))/(A(IQ,J)*SIN(U(IQ,II)))
      NI=N*(I-1)+IQ
      NIII=N*(I-1)+II
      NII=N*(I-1)+I
      NIJ=N*(I-1)+J
      Z(NI)=-Z(NIII)-Z(NII)-Z(NIJ)
      I=I+1
      J=J+1
      II=IQ
   11 CONTINUE
      GO TO 48
   47 J=1
      JJ=L
      GO TO 46
   48 CALL TRANS(TRAZ,Z,N,N)
      READ(1,20)(G(I),I=1,N)
      I=1
      DO 301 J=1,N
      AMAS(I)=G(J)
      AMAS(I)=1/AMAS(I)
      I=I+13
  301 CONTINUE
      CALL MPMATRIX(WORK,Z,AMAS,N,N,N)
      CALL MPMATRIX(G,WORK,TRAZ,N,N,N)
C READ THE NUMBER OF INTERNAL CO-ORDINATES INVOLVED IN THE ITH SYMMETRY
```

```
C CO-ORDINATE. THEN READ THE NUMBER(S) OF THE INTERNAL CO-ORDINATES.
      DO 14,IO=1,N
      READ(1,190)K
      READ(1,500)(IX(I),I=1,K)
      DO 14,I=1,K
      KE=IX(I)
      IF(KE)71,14,81
   14 CONTINUE
      GO TO 51
   71 IQ=-KE
      IQ=IQ+N*(IO-1)
      E(IQ)=-1/SQRT(FLOAT(K))
      GO TO 14
   81 IQ=KE
      IQ=IQ+N*(IO-1)
      E(IQ)=1/SQRT(FLOAT(K))
      GO TO 14
   51 CALL TRANS(TRAE,E,N,N)
      IF(KKKN-1) 54,53,54
C READ NUMBER OF FORCE CONSTANTS.
   53 READ(1,190)IRE
C READ FORCE CONSTANTS.
      READ(1,400)(ZPOT(I),I=1,IRE)
C READ THE NUMBER OF THE TIMES THE ITH FORCE CONSTANT OCCURS IN THE POTE TIAL
C ENERGY EXPRESSION THEN THE ROW AND COLUMN LABELS OF THE ITH ENTERY IN THE
C POTENTIAL ENERGY MATRIX.
      NO=1
      IJ=1
      DO 591,I=1,IRE
      READ(1,190)ID(I)
      KI=2*ID(I)
      IK=IJ+KI-1
      READ(1,100)(IZ(NO),NO=IJ,IK)
      IJ=IJ+KI
  591 CONTINUE
   54 NN=N*N
      CALL TWENTY6(ZPOT,N,IRE,F,ID,IZ)
      WRITE(2,2000)
```

```
C OUTPUT G=MATRIX IN TERMS OF INTERNAL CO-ORDINATES.
      WRITE(2,200)(G(I),I=1,144)
      CALL MPMATRIX(WORK,E,G,N,N,N)
      CALL MPMATRIX(GSYM,WORK,TRAE,N,N,N)
      WRITE(2,2010)
      WRITE(2,200)(GSYM(I),I=1,144)
      CALL FPEIGEN1(GSYM(1),N,0,0000001,0,WORK(1))
      WRITE(2,2030)
      WRITE(2,200)(GSYM(I),I=1,144)
      M=N-3
      DO 291,I=1,NN
      BB(I)=0.00000000000
  291 CONTINUE
      DO 15,I=1,N
      IN=N*(I-1)+I
      IF(GSYM(IN))991,16,16
   16 BB(IN)=SQRT(GSYM(IN))
   15 CONTINUE
      GO TO 17
  991 BB(IN)=SQRT(ABS(GSYM(IN)))
      GO TO 15
   17 CALL MPMATRIX(WOR1,BB,WORK,N,N,N)
      CALL MPMATRIX(B701,WOR1,E,N,N,N)
      CALL MPMATRIX(G,TRAZ,TRAE,N,N,N)
      CALL TRANS(WOR1,WORK,N,N)
      CALL MPMATRIX(TRAZ,AMAS,G,N,N,N)
      DO 391 I=1,N
      IN=N*(I-1)+I
      IF(ABS(BB(IN)).LT.0.0001) BB(IN)=1000000.0
      BB(IN)=1/BB(IN)
      DO 391 J=1,N
      JK=N*(J-1)+I
      WOR1(JK)=BB(IN)*WOR1(JK)
  391 CONTINUE
      CALL MPMATRIX(FSYM,TRAZ,WOR1,N,N,N)
```

```
      WRITE(2,2200)
      WRITE(2,200)(FSYM(I),I=1,NN)
      CALL TRANS(B801,B701,N,N)
      DO 811 I=1,NN
      AMAS(I)=0.00000000000
  811 CONTINUE
      WRITE(2,2100)
      WRITE(2,200)(B701(I),I=1,NN)
      CALL MPMATRIX(AMAS,B701,F,N,N,N)
      CALL MPMATRIX(FSYM,AMAS,B801,N,N,N)
      DO 7999 I=1,NN
      AMAS(I)=0.00000000
      E(I)=0.0000000000
 7999 CONTINUE
      CALL FPEIGEN1(FSYM(1),N,0.0001,0,G(1))
      WRITE(2,2040)
      WRITE(2,200)(FSYM(I),I=1,NN)
      WRITE(2,2050)
      DO 1111 I=1,N
      K=I+N*(I-1)
      WORK(I)=1302.9*SQRT(FSYM(K))
      WRITE(2,60)WORK(I)
 1111 CONTINUE
      IF(KKKN-NNKL)8808,8999,8999
 8999 STOP
      END
```

(INPLANE)

```
      MASTER INPLANE
      DIMENSION X(12),Y(12),A(12,12),B(12,12),C(12,12),U(12,12),Z(576),
     1E(576),G(576),GS(576),WORK(576),ZPOT(47),ID(47),IZ(360),
     1W(576),ANAM(2)
      API=3.1415926536/180.0
   10 FORMAT(I5)
   20 FORMAT(F12.6)
   30 FORMAT(6F8.4)
   60 FORMAT(F10.1)
  100 FORMAT(6F10.4)
  190 FORMAT(16I5)
  200 FORMAT(//(12F8.4))
  350 FORMAT(/(24F5.2))
  400 FORMAT(10F8.4)
  500 FORMAT(16I5)
  707 FORMAT(2I5,2F14.6)
  879 FORMAT(F8.4,F8.2)
  900 FORMAT(I5,F14.6,I5,F14.6,I5,F14.6)
  700 FORMAT(I5,2F14.6)
  800 FORMAT(2I5)
  850 FORMAT(2A8)
 2100 FORMAT(1H1,/25H B701***W-MATRIX*********)
 2010 FORMAT(1H1,/25H G-MATRIX INT. CO-ORDS.**)
 2020 FORMAT(1H1,/25H G-MATRIX SYM. CO-ORDS.**)
 2030 FORMAT(1H1,/25H DIAGONAL G-MATRIX*******)
 2040 FORMAT(1H1,/25H SYM SEC. EQN.***********)
 2050 FORMAT(1H1,/25H DIAG. SEC. EQN.*********)
 2060 FORMAT(1H1,/25H EIGEN-FREQUENCIES*******)
 2070 FORMAT(1H1,/25H CART. DISP. ************)
 2080 FORMAT(1H1,/25H U-MATRIX****************)
      L=12
      M=6
C READ 16-CHARECTER COMMENT
      READ(1,850)ANAM(1),ANAM(2)
      WRITE(2,850)ANAM(1),ANAM(2)
      N=L
      N2=2*N
```

```
      NAT=L
      ME=M+1
C READ X AND Y CO-ORDINATES OF NUCLEAR ATOMS.
      READ(1,30)(X(I),I=1,M)
      READ(1,30)(Y(I),I=1,M)
C WRITE STRUCTURAL DATA
C READ BOND LENGTHS AND BOND ANGLES IN ORDER 106,102,103,...ETC.
      J=M
      I=1
      DO 2,K=1,M
      READ(1,879)A(I,J),U(I,J)
      A(J,I)=A(I,J)
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      I=I+1
      J=I-1
    2 CONTINUE
      DO 4,I=1,M
      J=I+1
      IF(J-ME)5,6,5
    5 B(I,J)=(X(J)-X(I))/A(I,J)
      C(I,J)=(Y(J)-Y(I))/A(I,J)
      WRITE(2,707)I,J,B(I,J),C(I,J)
      B(J,I)=-B(I,J)
      C(J,I)=-C(I,J)
    4 CONTINUE
      GO TO 7
    6 J=1
      GO TO 5
    7 J=M
      L=1
      LI=1
      DO 8,I=1,M
      K=N2*(L-1)+LI
      II=I+1
      IF(I-M)9,11,9
    9 Z(K)=((A(I,J)-A(I,II)*COS(U(I,J)))*B(I,J)+(A(I,II)-A(I,J)*COS(U(I,
     1J)))*B(I,II))
      Z(K)=Z(K)/(A(I,J)*A(I,II)*SIN(U(I,J)))
```

```
      K=K+1
      Z(K)=((A(I,J)-A(I,II)*COS(U(I,J)))*C(I,J)+(A(I,II)-A(I,J)*COS(U(I,
     1J)))*C(I,II))
      Z(K)=Z(K)/(A(I,J)*A(I,II)*SIN(U(I,J)))
      KKJ=K-1
      J=I
      LI=LI+2
      L=L+1
    8 CONTINUE
      GO TO 12
   11 II=1
      GO TO 9
   12 J=M
      L=3
      IO=11
      DO 13,I=1,M
      K=24*(I-1)+L
      II=I+1
      IF(I-6)14,15,14
   14 Z(K)=(COS(U(I,J))*B(I,II)-B(I,J))/(A(I,II)*SIN(U(I,J)))
      K=K+1
      Z(K)=(COS(U(I,J))*C(I,II)-C(I,J))/(A(I,II)*SIN(U(I,J)))
      KKJ=K-1
      K=24*(I-1)+IO
      Z(K)=(COS(U(I,J))*B(I,J)-B(I,II))/(A(I,J)*SIN(U(I,J)))
      K=K+1
      Z(K)=(COS(U(I,J))*C(I,J)-C(I,II))/(A(I,J)*SIN(U(I,J)))
      L=L+2
      J=I
      IF(IO-11)16,17,16
   16 IO=IO+2
   13 CONTINUE
      GO TO 18
   15 II=1
      K=24*(I-1)+1
      GO TO 14
   17 IO=-1
```

```
      GO TO 16
   18 J=7
      DO 19,I=1,M
      READ(1,20)A(I,J)
      A(J,I)=A(I,J)
      J=J+1
   19 CONTINUE
      J=7
      DO 21,I=1,M
      READ(1,20)U(I,J)
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      J=J+1
   21 CONTINUE
      J=8
C READ BOND LENGTHS AND BOND ANGLES INVOLVING SUBTS. IN ORDER BOND LENGT  106
C BOND ANGLE 106, B.L. 102 B.A. 102,..... ETC.
      DO 22,I=1,M
      IF(I-6)23,24,23
   23 READ(1,20)U(I,J)
      U(I,J)=API*U(I,J)
      U(J,I)=U(I,J)
      J=J+1
   22 CONTINUE
      GO TO 25
   24 J=7
      GO TO 23
   25 ME=M+1
      L=NAT
C READ X AND Y CO-ORDINATES OF SUBSTITUENTS.
      READ(1,30)(X(I),I=ME,L)
      READ(1,30)(Y(I),I=ME,L)
      DO 27,I=1,M
      J=I+M
      B(I,J)=(X(J)-X(I))/A(I,J)
      C(I,J)=(Y(J)-Y(I))/A(I,J)
      B(J,I)=-B(I,J)
      C(J,I)=-C(I,J)
   27 CONTINUE
```

```
      J=7
      JJ=J
      IO=1
      K=145
      DO 28,I=1,M
      II=I+1
      IF(I-6)29,31,29
   29 Z(K)=((A(I,J)-A(I,II)*COS(U(I,J)))*B(I,J)+(A(I,II)-A(I,J)*COS(U(I,
     1J)),*B(I,II))/(A(I,II)*A(I,J)*SIN(U(I,J)))
      K=K+1
      Z(K)=((A(I,J)-A(I,II)*COS(U(I,J)))*C(I,J)+(A(I,II)-A(I,J)*COS(U(I,
     1J)))+C(I,II))/(A(I,II)*A(I,J)*SIN(U(I,J)))
      KKJ=K-1
      K=K+49
      J=J+1
      IO=IO+1
   28 JJ=JJ+2
      GO TO 32
   31 II=1
      GO TO 29
   32 J=8
      JJ=J
      IO=3
      K=171
      DO 33,I=1,M
      L=I+1
      II=I+1
      IF(I-6)34,35,34
   34 Z(K)=((A(L,J)-A(I,II)*COS(U(L,J)))*B(L,J)+(A(I,II)-A(L,J)*COS(U(I,
     1J)))*B(II,I))/(A(I,II)*A(L,J)*SIN(U(L,J)))
      K=K+1
      Z(K)=((A(L,J)-A(I,II)*COS(U(L,J)))*C(L,J)+(A(I,II)-A(L,J)*COS(U(I,
     1J)))*C(II,I))/(A(I,II)*A(L,J)*SIN(U(L,J)))
      KKJ=K-1
      J=J+1
      JJ=JJ+2
      IO=IO+1
      K=K+49
   33 CONTINUE
```

```
      GO TO 36
   35 II=1
      L=1
      J=I+1
      K=K-12
      GO TO 34
   36 J=M+1
      IR=J
      DO 37,I=1,M
      K=24*(J-1)+J
      II=I+1
      IF(I-M)38,39,38
   38 Z(K)=(COS(U(I,IR))*B(I,IR)-B(I,II))/(SIN(U(I,IR))*A(I,IR))
      K=K+1
      Z(K)=(COS(U(I,IR))*C(I,IR)-C(I,II))/(SIN(U(I,IR))*A(I,IR))
      JJ=J+1
      JI=J+2
      KE=(JJ-1)*24+JI
      IO=IR+1
      IF(I-M)41,42,41
   41 Z(KE)=(COS(U(I,IO))*B(II,IO)-B(II,I))/(SIN(U(I,IO))*A(II,IO))
      KS=KE+1
      Z(KS)=(COS(U(I,IO))*C(II,IO)-C(II,I))/(SIN(U(I,IO))*A(II,IO))
      J=J+2
      IR=IR+1
   37 CONTINUE
      GO TO 43
   39 II=1
      GO TO 38
   42 II=1
      KE=KE-2*I
      IO=I+1
      GO TO 41
   43 J=M+1
      JK=J
      JR=3
      JS=J+1
      JP=1
      IO=2
```

```
      IK=J+1
      K=24*(JK-1)+JR
      KE=24*(JS-1)+JD
      DO 44,I=1,M
      II=I+1
      IF(I-M)45,46,45
   45 Z(K)=(COS(U(I,J))*B(I,II)-B(I,J))/(SIN(U(I,J))*A(I,II))
      KKJ=K-1
      N=K+1
      Z(N)=(COS(U(I,J))*C(I,II)-C(I,J))/(SIN(U(I,J))*A(I,II))
      JJ=J+1
      IF(I-M)47,48,47
   47 Z(KE)=(COS(U(I,JJ))*B(II,I)-B(IO,IK))/(SIN(U(I,JJ))*A(II,I))
      NE=KE+1
      Z(NE)=(COS(U(I,JJ))*C(II,I)-C(IO,IK))/(SIN(U(I,JJ))*A(II,I))
      JK=JK+2
      JR=JR+2
      JS=JS+2
      JD=JD+2
      J=J+1
      IO=IO+1
      IK=IK+1
      K=24*(JK-1)+JR
      KE=24*(JS-1)+JD
   44 CONTINUE
      GO TO 49
   46 II=1
      JR=JR-2*I
      K=24*(JK-1)+JR
      GO TO 45
   48 II=1
      JJ=I+1
      IO=1
      IK=I+1
      GO TO 47
   49 J=M+1
      KM=3*M
      KQ=J+M
```

```
      IQ=24*(J-1)+KQ
      K=24*(KM-1)+J
      KI=24*(J-1)+J
      DO 51,I=1,M
      W(IQ)=(Z(K)-Z(KI))/2
      NQ=IQ+1
      KT=K+1
      KS=KI+1
      W(NQ)=(Z(KT)-Z(KS))/2
      J=J+2
      KI=24*(J-1)+J
      K=24*(J-2)+J
      IQ=IQ+26
   51 CONTINUE
      J=M+1
      IQ=1
      IS=1
      IK=3*M
      K=24*(IK-1)+IS
      IQ=24*(J-1)+IQ
      KI=IQ
      DO 52,I=1,M
      W(IQ)=(Z(K)-Z(KI))/2
      W(IQ+1)=(Z(K+1)-Z(KI+1))/2
      KI=KI+50
      K=KI-24
      IQ=IQ+26
   52 CONTINUE
      J=M+1
      IK=24*(J-1)+3
      IQ=IK
      DO 53,I=1,M
      IF(I-M)54,55,54
   54 W(IQ)=-(Z(IK))/2
      W(IQ+1)=-(Z(IK+1))/2
      IQ=IQ+26
      IK=IK+50
   53 CONTINUE
      GO TO 56
```

```
   55 IQ=24*(2*I-1)+1
      IK=24*(3*I-2)+1
      GO TO 54
   56 IQ=24*M+2*M-1
      K=24*(3*M-1)+2*M-1
      DO 57,I=1,M
      W(IQ)=(Z(K))/2
      W(IQ+1)=(Z(K+1))/2
      K=24*(M+2*I-1)+2*I-1
      IQ=24*(M+I)+2*I-1
   57 CONTINUE
      DO 58,I=145,500
      Z(I)=W(I)
   58 CONTINUE
      N=24
      K=2*N*M+1
      KE=K+2
      DO 59,I=1,M
      II=I+1
      IF(I-M)61,62,61
   61 Z(K)=B(II,I)
      Z(K+1)=C(II,I)
      Z(KE)=B(I,II)
      Z(KE+1)=C(I,II)
      K=K+26
      KE=KE+26
   59 CONTINUE
      GO TO 63
   62 II=1
      KE=N*(3*I-1)+1
      GO TO 61
   63 K=N*M*3+1
      J=M+1
      IQ=1
      DO 64,I=1,M
      Z(K)=B(J,IQ)
      Z(K+1)=C(J,IQ)
```

```
      IQ=IQ+1
      J=J+1
   64 CONTINUE
      J=N+1
      K=3*N*M+13
      IQ=1
      DO 65,I=1,M
      Z(K)=B(IQ,J)
      Z(K+1)=C(IQ,J)
      IQ=IQ+1
      J=J+1
      K=K+N+2
   65 CONTINUE
      L=N
      LL=L*L
      L1=L+1
      READ(1,100)(GS(I),I=1,N)
      DO 333 K=1,N
      DO 333 I=1,N
      L=N*(K-1)+I
      WORK(L)=Z(L)/GS(I)
      LM=N*(I-1)+K
      W(LM)=Z(L)/GS(I)
  333 CONTINUE
      NN=N*N
      WRITE(2,2090)
      WRITE(2,200)(Z(I),I=1,NN)
      CALL MPMATRIX(G,WORK,Z,N,N,N,1)
C OUTPUT G-MATRIX IN TERMS OF INTERNAL CO-ORDINATES.
      WRITE(2,2010)
      WRITE(2,200)(G(I),I=1,NN)
C READ THE NUMBER OF INTERNAL CO-ORDINATES INVOLVED IN THE ITH SYMMETRY
      DO 9914 IO=1,N
      READ(1,10)K
C CO-ORDINATE. THEN READ THE NUMBER(S) OF THE INTERNAL CO-ORDINATES.
      READ(1,500)(IZ(I),I=1,K)
      DO 9914 I=1,K
      KE=IZ(I)
      IF(KE) 9971,9914,9981
 9914 CONTINUE
      GO TO 73
```

```
 9971 IQ=-KE
      IQ=IQ+N*(IQ-1)
      E(IQ)=-1/SQRT(FLOAT(K))
      GO TO 9914
 9981 IQ=KE
      IQ=IQ+N*(IQ-1)
      E(IQ)=1/SQRT(FLOAT(K))
      GO TO 9914
   73 CALL MPMATRIX(WORK,E,G,N,N,N,0)
      CALL MPMATRIX(GS,WORK,E,N,N,N,1)
      WRITE(2,2080)
      WRITE(2,200)(E(I),I=1,NN)
      WRITE(2,2020)
      WRITE(2,200)(GS(I),I=1,LL)
      CALL FPEIGEN1(GS(1),N,0.0000001,0,WORK(1))
      WRITE(2,2030)
      WRITE(2,200)(GS(I),I=1,LL)
      M=N-3
      DO 8915 I=1,N
      IN=N*(I-1)+I
      IF(GS(IN))9991,9916,9916
 9916 GS(IN)=SQRT(GS(IN))
 8915 CONTINUE
      GO TO 9917
 9991 GS(IN)=0.00000000
      GO TO 8915
 9917 CALL MPMATRIX(G,W,E,N,N,N,1)
      DO 8916 I=1,N
      IN=N*(I-1)+I
      NJ=N*(I-1)+1
      NJI=NJ+N-1
      DO 8918 J=NJ,NJI
      Z(J)=GS(IN)*WORK(J)
 8918 CONTINUE
      IN=N*(I-1)+I
      DO 8939 J=1,N
      NJ=N*(I-1)+J
      W(NJ)=GS(IN)*WORK(NJ)
 8939 CONTINUE
 8916 CONTINUE
      CALL MPMATRIX(WORK,Z,E,N,N,N,0)
      CALL MPMATRIX(GS,G,W,N,N,N,0)
```

```
C OUVPUT W-MATRIX.
      WRITE(2,2100)
      WRITE(2,200)(WORK(I),I=1,NN)
      WRITE(2,2070)
      WRITE(2,200)(GS(I),I=1,NN)
C READ NUMBER OF FORCE CONSTANTS.
 9951 READ(1,10)IRE
C READ FORCE CONSTANTS.
      READ(1,400)(ZPOT(I),I=1,IRE)
      NO=1
      IJ=1
C READ THE NUMBER OF TIMES THE ITH FORCE CONSTANT OCCURS IN THE POTENTIA
C ENERGY EXPRESSION THEN THE ROW AND COLUMN LABELS OF THE ITH ENTERY IN THE
C POTENTIAL ENERGY MATRIX.
      DO 591,I=1,IRE
      READ(1,190)ID(I)
      KI=2*ID(I)
      IK=IJ+KI-1
      READ(1,190)(IZ(NO),NO=IJ,IK)
      IJ=IJ+KI
  591 CONTINUE
 9954 NN=N*N
      DO 8919 I=1,NN
      G(I)=0.00000000
 8919 CONTINUE
      CALL TWENTY6(ZPOT,N,IRE,G,ID,IZ)
      CALL MPMATRIX(Z,E,G,N,N,N,0)
      CALL MPMATRIX(GS,Z,E,N,N,N,1)
      CALL MPMATRIX(Z,WORK,G[illegible],N,N,N,0)
      CALL MPMATRIX(G,Z,WORK,N,N,N,1)
      WRITE(2,2040)
      WRITE(2,200)(G(I),I=1,NN)
      CALL FPEIGEN1(G(1),N,0.0001,0,G(1))
      WRITE(2,2050)
      WRITE(2,350)(G(I),I=1,NN)
      WRITE(2,2060)
      DO 1111 I=1,N
      K=I+N*(I-1)
      WORK(I)=1302.9*SQRT(ABS(GS(K)))
      WRITE(2,60)WORK(I)
 1111 CONTINUE
  999 STOP
      END
```

```
      SUBROUTINE TWENTY6(ZPOT,XPOT,YPOT,N,IRE,F,ID,IZ)
      DIMENSION ZPOT(30),XPOT(30),YPOT(30),ID(30),IZ(300),F(144)
      I=1
      DO 2,J=1,IRE
      ZPOT(I)=YPOT(J)*XPOT(J)
      I=I+1
    2 CONTINUE
      NO=1
      IL=1
      DO 26,I=1,IRE
      DO 27,L=1,ID(I)
      IF(IZ(NO))28,29,29
   29 NE=N*(IZ(NO)-1)+IZ(NO+1)
      ME=N*(IZ(NO+1)-1)+IZ(NO)
      F(NE)=IL*ZPOT(I)
      F(ME)=F(NE)
      IF(ILL) 24,23,23
   23 NO=NO+2
      IL=1
      ILL=1
   27 CONTINUE
   26 CONTINUE
      GO TO 25
   28 IL=-1
      IZ(NO)=-IZ(NO)
      ILL=-1
      GO TO 29
   24 IZ(NO)=-IZ(NO)
      GO TO 23
   25 RETURN
      END
```

```
      SUBROUTINE MPMATRIX(D,A,B,I1,I2,I3)
      DIMENSION D(225),A(225),B(225)
      DO 1 I=1,I1
      DO 2 J=1,I3
      IK=I3*(I-1)+J
      D(IK)=0.0
      DO 3 K=1,I2
      II=I3*(K-1)+J
      IJ=I2*(I-1)+K
      D(IK)=D(IK)+A(IJ)*B(II)
    3 CONTINUE
    2 CONTINUE
    1 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE TRANS(T,A,N,M)
      DIMENSION T(225),A(225)
      DO 1 I=1,N
      DO 2 J=1,M
      IN=N*(I-1)+J
      IM=M*(J-1)+I
      T(IM)=A(IN)
    2 CONTINUE
    1 CONTINUE
      RETURN
      END
```

(BEDCOMII)

```
      MASTER BEDCOMII
      DIMENSION B701(225),B801(225),XPOT(30),XINIT(30),IOBS(20)
     1,WAIT(20),ICO(20),YPOT(30),FPOT(30),OUT4(20),EX(100),
     1ZPOT(30),CORR(20),YACO(50),WORK(144),CALC(20),CAL1(13),
     1IZ(300),G(225),ER1(14),IH(20),AB(30),WI(30),WOR1(225),WOR2(225),
     1ID(30),OBS(14),VEC(225),IAR(30),ER(18),PED(40),VAR(20),COR(30)
     1,DES(10),ICX(10)
   10 FORMAT(I3)
   20 FORMAT(F8.5)
  100 FORMAT(16I5)
   90 FORMAT(I5)
  310 FORMAT(//11H PARAMETERS)
  320 FORMAT(//(53H*****************************************************
     1))
  330 FORMAT(4H *  ,I5,2F8.1,4X,A8,2X.F8.1,6H     *)
  340 FORMAT(//(I5,2F8.4)//)
  370 FORMAT(I5,2F12.4)
  380 FORMAT((34H**************************AVERAGE=,F5.1,14H ***********
     1**)//)
  400 FORMAT(14I5)
  420 FORMAT(//(9F8.4))
  600 FORMAT(6F8.4)
  610 FORMAT(10F8.4)
  620 FORMAT(10I5)
  650 FORMAT(5H PED.)
  660 FORMAT(I5,F10.2,2X,(8(I5,I3)))
  670 FORMAT(//(12F8.4))
  680 FORMAT(I5,6F8.4)
  690 FORMAT(I5,11F6.0)
 1600 FORMAT(//7H CORREL/(12F8.4))
 1610 FORMAT(23H TOUGH PARAMETERS CYCLE,I5,22H SKIPPED OUT,FREQ. NO.,I5)
 1700 FORMAT(//4H VAR/(12F8.4))
 1990 FORMAT(1H1,//(10H ITERATION,I5,6H CYCLE,I5)/)
 2000 FORMAT(1H1,//(17H HISTORY OF CYCLE,I4)//)
 2001 FORMAT(17H  YACO/OBS/WAIT//)
 2002 FORMAT(1H1,(//16H LSM CALCULATION)//)
 2010 FORMAT(9F8.4)
```

```
2020 FORMAT(18H BEST SET IS NO.  ,I5)
2030 FORMAT(4I5)
2040 FORMAT(11X,11F6.0)
2050 FORMAT(1H1,(100H**************************************************
    1**************************************************))
2060 FORMAT(/(5H     )/)
2070 FORMAT(I5,8F8.4)
2080 FORMAT(17H VAR UNOBTAINABLE)
2090 FORMAT(/5H CHI=,F12.5)
2190 FORMAT(9F8.4)
3010 FORMAT(1H1,/(11H CART. DIS.)/)
3290 FORMAT(10A8)
     WRITE(2,2002)
     READ(1,620) N,IH49,ICAR,IDIV,IREF,MARY
     NN=N*N
     M=N-3
     MN=M*N
     NM=MN
     MM=M*M
     L=1
     J=L+N-1
     DO 777 I=1,M
     READ(1,600)(B701(K),K=L,J)
     L=L+N
     J=L+N-1
 777 CONTINUE
     WRITE(2,600)(B701(I),I=1,MN)
     CALL TRANS(B801,B701,M,N)
     READ(1,2030)(IH(I),I=1,IH49)
     READ(1,400)IC31,IC01
     IRE=IC01
     READ(1,610)(XINIT(I),I=1,IRE)
     DO 27 I=1,IRE
     XPOT(I)=XINIT(I)
  27 CONTINUE
     IJ=1
     DO 26 I=1,IRE
```

```
      READ(1,90)ID(I)
      IAR(I)=IJ
      IKKK=2*ID(I)
      KIII=IJ+IKKK-1
      READ(1,100)(IZ(NO),NO=IJ,KIII)
      WRITE(2,660)I,XINIT(I),(IZ(JJJ),JJJ=IJ,KIII)
      IJ=IJ+IKKK
   20 CONTINUE
      READ(1,400)(IOBS(I),I=1,M)
      READ(1,3290)(DES(I),I=1,M)
      DO 5,I=1,M
      OBS(I)=(IOBS(I)**2)/(1302.9**2)
      WAIT(I)=1/OBS(I)
    5 CONTINUE
      READ(1,90)IK
      IS=0
    7 IS=IS+1
      WRITE(2,2050)
      M=N-3
      DO 4 I=1,IRE
      YPOT(I)=1.0
    4 CONTINUE
      READ(1,400)(ICX(I),I=1,14)
      IC=ICX(1)
      ISS=ICX(2)
      DO 1 I=1,IC
      ICO(I)=ICX(I+2)
    1 CONTINUE
      DO 9 I=1,IC
      J=ICO(I)
      YPOT(J)=XINIT(J)
      XPOT(J)=1.0
      J=(I-1)*(ISS+2)+1
      FPOT(J)=ICO(I)
      FPOT(J+1)=YPOT(ICO(I))
    9 CONTINUE
      CALL TWENTY6(ZPOT,XPOT,YPOT,N,IRE,G,ID,IZ)
```

```
      CALL MPMATRIX(WORK,B701,G,M,N,N)
      CALL MPMATRIX(WOR1,WORK,B801,M,N,M)
      WRITE(2,420)(WOR1(I),I=1,MM)
      CALL SEVENTY2(WOR1,CALC,M,IH49,IH,VEC)
      WRITE(2,420)(VEC(I),I=1,MM)
      CALL MPMATRIX(WOR2,VEC,B701,M,M,N)
      WRITE(2,2190)(WOR2(I),I=1,MN)
      CALL TRANS(WOR1,WOR2,M,N)
      CALL MPMATRIX(WORK,WOR2,G,M,N,N)
      CALL MPMATRIX(VEC,WORK,WOR1,M,N,M)
      WRITE(2,420)(VEC(I),I=1,MM)
      XEEE=0.0
      DO 288 I=1,IC
      J=ICO(I)
      WRITE(2,340)J,YPOT(J)
  288 CONTINUE
      WRITE(2,320)
      DO 225 I=1,M
      WOR1(1)=1302.9*SQRT(ABS(CALC(I)))
      IF(CALC(I)) 264,265,265
  265 XE=IOBS(I)
      J=(ISS+3)*(I-1)+1
      EX(J)=I
      EX(J+1)=IOBS(I)
      EX(J+2)=WOR1(1)
      XEE=WOR1(1)-XE
      XEEE=XEEE+ABS(XEE)
      WRITE(2,330)I,XE,WOR1(1),DES(I),XEE
  225 CONTINUE
      XEEE=XEEE/M
      WRITE(2,380)XEEE
      OUT4(1)=XEEE
      DO 226 JJ=1,M
      DO 222 I=1,IC
      KK=M*(I-1)+JJ
      K=ICO(I)
      NO=IAR(K)
      ISI=1
      LM=2
      YACO(KK)=0.0
      NA=ID(K)
      IF(IZ(NO).EQ.IZ(NO+1)) LM=1
      DO 921 JI=1,NA
      MD=IZ(NO)
      MS=IZ(NO+1)
      IF(MD.LT.0) ISI=-1
      IF(MD.LT.0) MD=-MD
      IM=N*(JJ-1)+MD
      IN=N*(JJ-1)+MS
      YACO(KK)=YACO(KK)+ISI*WOR2(IM)*WOR2(IN)
      NO=NO+2
      ISI=1
  921 CONTINUE
      YACO(KK)=LM*YACO(KK)
      LM=2
  222 CONTINUE
  226 CONTINUE
      WRITE(2,2001)
```

```
      ICM2=IC*M
      WRITE(2,2010)(YACO(I),I=1,ICM2)
      WRITE(2,2010)(OBS(I),I=1,M)
      WRITE(2,2010)(WAIT(I),I=1,M)
      ICM=IC*M
      IF(IREF) 281,282,281
  282 DO 14 IOO=1,ISS
      WRITE(2,1990)IOO,IS
      DO 15,I=1,M
      ER1(I)=(CALC(I)-OBS(I))/IDIV
   15 CONTINUE
      DO 22,I=1,IC
      DO 42,JN=1,M
      J=M*(I-1)+JN
      WORK(J)=YACO(J)*WAIT(JN)
   42 CONTINUE
   22 CONTINUE
      DO 901,I=1,IC
      DO 902,J=1,IC
      KI=IC*(I-1)+J
      WOR1(KI)=0.0
      DO 903,K=1,M
      II=M*(I-1)+K
      IJ=IC*(K-1)+J
      IJ=M*(J-1)+K
      WOR1(KI)=WOR1(KI)+WORK(II)*YACO(IJ)
  903 CONTINUE
  902 CONTINUE
  901 CONTINUE
      ICIC=IC*IC
      CALL TRANS(WOR2,WOR1,IC,IC)
      DO 444,I=1,ICIC
      WOR1(I)=0.0
  444 CONTINUE
      DO 445,I=1,IC
      ITS=IC*(I-1)+I
```

```
      WOR1(ITS)=1.0
  445 CONTINUE
      I=ICIC
      IN=1
      CALL F4ACSL(WOR2,WOR1,IC,I,I,IN,VEC,D,IDD,ITT,AB,WI,ZPOT)
      WRITE(2,2010)(VEC(I),I=1,ICIC)
      WRITE(2,310)
      DO 904,I=1,IC
      WOR2(I)=0.0
      WOR1(I)=0.0
      DO 905,J=1,M
      II=M*(I-1)+J
      WOR2(I)=WOR2(I)+WORK(II)*ER1(J)
      WOR1(I)=WOR1(I)+WORK(II)*ER1(J)*IDIV
  905 CONTINUE
  904 CONTINUE
      DO 906,I=1,IC
      WORK(I)=0.0
      AB(I)=0.0
      DO 907,J=1,IC
      II=IC*(I-1)+J
      WORK(I)=WORK(I)+VEC(II)*WOR2(J)
      AB(I)=AB(I)+VEC(II)*WOR2(J)
  907 CONTINUE
  906 CONTINUE
      DO 17 I=1,IC
      CORR(I)=-WORK(I)
      ZPOT(I)=-AB(I)
      IP=ICO(I)
      XE=YPOT(IP)
      YPOT(IP)=XE+CORR(I)
      WRITE(2,340)IP,XE,YPOT(IP)
      J=(I-1)*(ISS+2)+I00+2
      FPOT(J)=YPOT(IP)
   17 CONTINUE
      M=N-3
      DO 229 J=1,M
```

```
      ER(J)=0.0000000
      DO 228 I=1,IC
      II=M*(I-1)+J
      ER(J)=ER(J)+ZPOT(I)*YACO(II)
  228 CONTINUE
      ER(J)=ER(J)-ER1(J)*IDIV
  229 CONTINUE
      XE=0.0
      DO 251 I=1,M
      XE=XE+WAIT(I)*(ER(I)**2)
  251 CONTINUE
      WRITE(2,2090)XE
  269 DO 253 J=1,M
      DO 252 I=1,IC
      II=IC*(J-1)+I
      IJ=M*(I-1)+J
      PED(II)=(YACO(IJ)/CALC(J))*XINIT(ICO(I))
  252 CONTINUE
  253 CONTINUE
      WRITE(2,650)
      WRITE(2,670)(PED(I),I=1,ICM)
      IF(IREF) 273,284,273
  284 DO 256 I=1,IC
      DO 257 J=1,IC
      IJ=IC*(I-1)+J
      II=IC*(I-1)+I
      JJ=IC*(J-1)+J
      VECC=VEC(II)*VEC(JJ)
      IF(VECC) 259,259,258
  258 COR(IJ)=VEC(IJ)/SQRT(VECC)
  257 CONTINUE
  256 CONTINUE
      GO TO 261
  259 WRITE(2,2080)
      GO TO 262
  261 WRITE(2,1600)(COR(I),I=1,ICIC)
  262 DO 254 I=1,IC
```

```
      II=IC*(I-1)+I
      VAR(I)=VEC(II)*XE/(IRE-M)
  254 CONTINUE
      WRITE(2,1700)(VAR(I),I=1,IC)
      CALL TWENTY6(ZPOT,XPOT,YPOT,N,IRE,G,ID,IZ)
      CALL MPMATRIX(WORK,B701,G,M,N,M)
      CALL MPMATRIX(WOR1,WORK,B801,M,M,M)
      CALL SEVENTY2(WOR1,CALC,M,IM49,IM,VEC)
      CALL MPMATRIX(WOR2,VEC,B701,M,M,N)
      WRITE(2,320)
      XEEE=0.0
      DO 325 I=1,M
      WOR1(1)=1302.9*SQRT(ABS(CALC(I)))
      IF(CALC(I)) 266,267,267
  267 XE=IOBS(I)
      J=(I-1)*(ISS+3)+I00+3
      EX(J)=WOR1(1)
      XEE=WOR1(1)-XE
      WRITE(2,330)I,XE,WOR1(1),DES(I),XEE
      XEEE=XEEE+ABS(XEE)
  325 CONTINUE
      XEEE=XEEE/M
      OUT4(I00+1)=XEEE
      WRITE(4,380)XEEE
      DO 326 JJ=1,M
      DO 322 I=1,IC
      KK=M*(I-1)+JJ
      K=ICO(I)
      NO=IAK(K)
      ISI=1
      LM=2
      YACO(KK)=0.0
      NA=ID(K)
      IF(IZ(NO).EQ.IZ(NO+1)) LM=1
      DO 925 JI=1,NA
      MD=IZ(NO)
      MS=IZ(NO+1)
      IF(MD.LT.0) ISI=-1
      IF(MD.LT.0) MD=-MD
      IM=N*(JJ-1)+MD
      IN=N*(JJ-1)+MS
      YACO(KK)=YACO(KK)+ISI*WOR2(IM)*WOR2(IN)
      NO=NO+2
      ISI=1
  925 CONTINUE
      YACO(KK)=LM*YACO(KK)
      LM=2
  322 CONTINUE
  326 CONTINUE
   14 CONTINUE
      WRITE(2,2000)IS
      DO 75 I=1,IC
```

```
      J=(I-1)*(ISS+2)+1
      L=INT(FPOT(J))
      J1=J+1
      J2=J1+ISS
      WRITE(2,680)L,(FPOT(J),J=J1,J2)
   75 CONTINUE
      DO 76 I=1,N
      J=(I-1)*(ISS+3)+1
      L=INT(EX(J))
      J1=J+1
      J2=J1+ISS+1
      WRITE(2,690)L,(EX(J),J=J1,J2)
   76 CONTINUE
      INO=ISS
  271 CALL MINI(OUT4,INO,KKK)
      ISS1=INO+1
      WRITE(2,2040)(OUT4(I),I=1,ISS1)
      WRITE(2,2020)KKK
  273 DO 18 I=1,IRE
      XPOT(I)=XINIT(I)
   18 CONTINUE
      IF(IREF) 551,552,551
  552 IF(IC31-4049) 551,19,551
  551 IF(IS-IK)7,374,374
  374 IF(ICAR) 74,74,72
   72 READ(1,2010)(WOR1(I),I=1,MN)
      WRITE(2,2010)(WOR1(I),I=1,MN)
      CALL TRANS(WORK,VEC,M,M)
      CALL MPMATRIX(WOR2,WOR1,WORK,N,M,M)
      WRITE(2,3010)
      WRITE(2,2010)(WOR2(I),I=1,MN)
      IF(MARY.EQ.0) GO TO 74
      CALL MARI(WOR2,N)
      GO TO 74
   19 DO 21,I=1,IC
      K=KKK+(I-1)*(ISS+2)+1
      IP=ICO(I)
      XINIT(IP)=FPOT(K)
      XPOT(IP)=XINIT(IP)
   21 CONTINUE
      WRITE(2,610)(XPOT(I),I=1,IRE)
      GO TO 551
      GO TO 268
  264 WOR1(1)=-WOR1(1)
      WRITE(2,1610)IS,I
      INO=1
      GO TO 273
  266 WOR1(1)=-WOR1(1)
      WRITE(2,1610)IS,I
      INO=INO+1
      GO TO 271
  281 WRITE(2,2010)(YACO(I),I=1,ICM2)
      GO TO 269
   74 WRITE(2,10)N
      WRITE(2,610)(XINIT(I),I=1,IRE)
  268 STOP
      END
```

```
      SUBROUTINE SEVENTY2(WORK,CALC,M,IH49,IH,VEC)
      DIMENSION WORK(169),F(20),CALC(20),IH(20),WOR2(30),VEC(169)
   90 FORMAT(2I5)
      N=M+3
      L=1
      NN=N*N
      MN=M*(M+3)
      MM=M*M
      KN=1
      DO 37,ID=1,IH49
      IN=1
      NI=IN
      K=IH(ID)
      LL=K+L-1
      DO 35,LLL=L,LL
      DO 36,LLLL=L,LL
      IPE=M*(LLL-1)+LLLL
      F(IN)=WORK(IPE)
      IN=IN+1
   36 CONTINUE
   35 CONTINUE
      L=LL+1
      IF(K-1)39,41,39
   39 IPE=K*K
      CALL FPEIGEN1(F(1),K,0.0001,0,WOR2(1);
   44 DO 38,IR=1,K
      KE=(IR-1)*K+IR
      CALC(KN)=F(KE)
      KN=KN+1
   38 CONTINUE
      KNN=KN-1
      KK=1
      IZ=(KNN-K)*M+KN-K
      DO 33 II=1,K
      DO 34 JJ=1,K
      VEC(IZ)=WOR2(KK)
      KK=KK+1
      IZ=IZ+1
   34 CONTINUE
      IZ=IZ+M-K
   33 CONTINUE
   37 CONTINUE
      GO TO 46
   41 WOR2(1)=1.0
      GO TO 44
   46 RETURN
      END
```

```
      SUBROUTINE MINI(O,M,K)
      DIMENSION O(20)
      KK=1
      DO 1 I=2,M
      IF(O(KK)-O(I))1,1,3
    1 CONTINUE
      K=KK
      GO TO 4
    3 KK=I
      GO TO 1
    4 RETURN
      END
```

(OFBQ091)

```
      MASTER OFBQ091
      DIMENSION G(144),FPOT(30),ICO(20),ID(30),IZ(200),XINIT(30),
     1OBS(45),WI(49),WOR1(144),WORK(144),B702(144),CAL3(45),
     1XPOT(30),YPOT(30),ZPOT(49),AB(49),B701(144),CALC(45),
     1VEC1(144),IAR(30),B703(144),B704(144),
     1B705(576),IH49(5),IH1(4),IH2(4),IH3(4),IH4(4),IH5(4),
     1WOR3(144),YACO(315),CAL1(45),CORR(45),ER1(45),WOR2(144)
     1,UI(20),EX(350),PED(315)
      COMMON WOR1,YACO,ID,IZ,M,IAR,ICO,N,IC,MISM,CAL1,CAL3
   10 FORMAT(I5)
   20 FORMAT(F8.5)
   40 FORMAT(F12.6)
   90 FORMAT(2I5)
  100 FORMAT(16I5)
  200 FORMAT(/(12F8.4))
  240 FORMAT(F8.1)
  250 FORMAT(//3F12.6)
  320 FORMAT(//(45H*********************************************))
  330 FORMAT(4H *  ,I5,2F8.1,6X,F8.1,10F7.3,6H     *)
  340 FORMAT(I5,2F8.4)
  380 FORMAT((34H**************************AVERAGE=,F5.1,6H *****)//)
  600 FORMAT(6F8.4)
  610 FORMAT(10F8.4)
  620 FORMAT(2I5)
  630 FORMAT(10I5)
  680 FORMAT(I5,11F8.4)
  690 FORMAT(I5,11F6.0)
  780 FORMAT(///(3F8.4))
  790 FORMAT(9F8.5)
  990 FORMAT(/9F10.4)
 2010 FORMAT(1H1,(20H LSM CALCULATION    )/)
 2020 FORMAT(I5,2X,F8.4,16I5)
 2030 FORMAT(9I5)
 2040 FORMAT(18H BEST SET IS NO.   ,I5,5X,11F6.0)
 2050 FORMAT(9F8.1)
      READ(1,630)N,ISO,ISYM,IDIV
```

```
      NN=N*N
      M=N-3
      MN=M*N
      NM=MN
      READ(1,600)(B701(I),I=1,MN)
      READ(1,600)(B702(I),I=1,MN)
      READ(1,600)(B703(I),I=1,MN)
      READ(1,600)(B704(I),I=1,MN)
      READ(1,600)(B705(I),I=1,MN)
      READ(1,2030)(IH49(I),I=1,ISYM)
      READ(1,2030)(IH1(I),I=1,IH49(1))
      READ(1,2030)(IH2(I),I=1,IH49(2))
      READ(1,2030)(IH3(I),I=1,IH49(3))
      READ(1,2030)(IH4(I),I=1,IH49(4))
      READ(1,2030)(IH5(I),I=1,IH49(5))
      READ(1,90)IC31,IC01
      IRE=IC01
      READ(1,610)(XINIT(I),I=1,IRE)
      NO=1
      WRITE(2,2010)
      DO 27 I=1,IRE
      XPOT(I)=XINIT(I)
   27 CONTINUE
      IJ=1
      DO 26 I=1,IRE
      READ(1,90)ID(I)
      IAR(I)=IJ
      IKKK=2*ID(I)
      KIII=IJ+IKKK-1
      READ(1,100)(IZ(NO),NO=IJ,KIII)
      WRITE(2,2020)I,XINIT(I),(IZ(NO),NO=IJ,KIII)
      IJ=IJ+IKKK
   26 CONTINUE
      MISM=ISYM*M
      READ(1,2050)(OBS(I),I=1,MISM)
      DO 5 I=1,MISM
      OBS(I)=(OBS(I)**2)/(1302.9**2)
    5 CONTINUE
```

```
      READ(1,10)IK
      IS=0
    7 IS=IS+1
      DO 4 I=1,IC01
      YPOT(I)=1.0
    4 CONTINUE
      READ(1,100)IC,ISS
      READ(1,100)(ICO(I),I=1,IC)
      DO 9 I=1,IC
      J=ICO(I)
      XPOT(J)=1.0
      YPOT(J)=XINIT(J)
      JK=(I-1)*(ISS+2)+1
      FPOT(JK)=J
      FPOT(JK+1)=YPOT(J)
    9 CONTINUE
      CALL TWENTY6(XPOT,YPOT,N,IRE,G,ID,IZ)
      CALL MPMAT(WORK,B701,G,M,N,N,0)

      CALL MPMAT(WOR3,WORK,B701,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(1),IH1,VEC1)
      CALL MPMAT(WOR1,VEC1,B701,M,M,N,0)
      J=0
      CALL JACOB(J)
      CALL MPMAT(WORK,B702,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B702,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(2),IH2,VEC1)
      CALL MPMAT(WOR1,VEC1,B702,M,M,N,0)
      J=1
      CALL JACOB(J)
      CALL MPMAT(WORK,B703,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B703,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(3),IH3,VEC1)
      CALL MPMAT(WOR1,VEC1,B703,M,M,N,0)
      J=2
      CALL JACOB(J)
      CALL MPMAT(WORK,B704,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B704,M,N,M,1)
```

```
      CALL SEVENTY2(WOR3,CAL3,M,IH49(4),IH4,VEC1)
      CALL MPMAT(WOR1,VEC1,B704,M,M,N,0)
      J=3
      CALL JACOB(J)
      CALL MPMAT(WORK,B705,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B705,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(5),IH5,VEC1)
      CALL MPMAT(WOR1,VEC1,B705,M,M,N,0)
      J=4
      CALL JACOB(J)
      M2=MISM
      WRITE(2,610)(CAL1(I),I=1,MISM)
      ICHS=IC*M2
      WRITE(2,610)(YACO(I),I=1,ICHS)
      DO 253 J=1,MISM
      DO 252 I=1,IC
      II=IC*(J-1)+I
      IJ=MISM*(I-1)+J
      PED(II)=(YACO(IJ)/CAL1(J))*XINIT(ICO(I))
  252 CONTINUE
  253 CONTINUE
      WRITE(2,320)
      XEEE=0.0
      DO 225 I=1,M2
      WOR1(1)=1302.9*SQRT(ABS(CAL1(I)))
      IF(CAL1(I)) 264,265,265
  265 XE=1302.9*SQRT(OBS(I))
       J=(ISS+3)*(I-1)+1
       EX(J)=I
       EX(J+1)=XE
       EX(J+2)=WOR1(1)
       XEE=WOR1(1)-XE
       XEEE=XEEE+ABS(XEE)
       J=IC*(I-1)+1
       JK=J+IC-1
       WRITE(2,330)I,XE,WOR1(1),XEE,(PED(IN),IN=J,JK)
  225  CONTINUE
```

```
      XEEE=XEEE/M2
      OI(1)=XEEE
      WRITE(2,380)XEEE
      ICM=IC*M
      ICN=IC*N
      ICMS=IC*MISM
      ICIC=IC*IC
      DO 14 IOO=1,ISS
      DO 15 I=1,MISM
      ER1(I)=(CAL1(I)-OBS(I))/IDIV
   15 CONTINUE
      DO 22 I=1,IC
      DO 42 IN=1,MISM
      J=MISM*(I-1)+IN
      WORK(J)=YACO(J)/OBS(IN)
   42 CONTINUE
   22 CONTINUE
      DO 901 I=1,IC
      DO 902 J=1,IC
      KI=IC*(I-1)+J
      WOR1(KI)=0.0
      DO 903 K=1,MISM
      II=MISM*(I-1)+K
      IJ=MISM*(J-1)+K
      WOR1(KI)=WOR1(KI)+WORK(II)*YACO(IJ)
  903 CONTINUE
  902 CONTINUE
  901 CONTINUE
      DO 444 I=1,ICIC
      WOR2(I)=0.0
  444 CONTINUE
      DO 445 I=1,IC
      ITS=IC*(I-1)+I
      WOR2(ITS)=1.0
  445 CONTINUE
      I=ICIC
```

```
      IN=1
      IF(IC-1) 333,339,333
  333 CALL F4ACSL(WOR1,WOR2,IC,I,I,IN,VEC1,D,IKK,ITT,AB,WI,ZPOT)
      GO TO 338
  339 VEC1(1)=1/WOR1(1)
  338 DO 904 I=1,IC
      WOR2(I)=0.0
      DO 905 J=1,MISM
      II=MISM*(I-1)+J
      WOR2(I)=WOR2(I)+WORK(II)*ER1(J)
  905 CONTINUE
  904 CONTINUE
      DO 906 I=1,IC
      WORK(I)=0.0
      DO 907 J=1,IC
      II=IC*(I-1)+J
      WORK(I)=WORK(I)+VEC1(II)*WOR2(J)
  907 CONTINUE
  906 CONTINUE
      DO 916 I=1,ICIC
      VEC1(I)=0.00000000
  916 CONTINUE
      DO 16 I=1,IC
      CORR(I)=-WORK(I)
      IP=ICO(I)
      XE=YPOT(IP)
      YPOT(IP)=XE+CORR(I)
      J=(I-1)*(ISS+2)+IOO+2
      FPOT(J)=YPOT(IP)
      WRITE(2,340)IP,XE,YPOT(IP)
   16 CONTINUE
```

```
      CALL TWENTY6(XPOT,YPOT,N,IRE,G,ID,IZ)
      CALL MPMAT(WORK,B701,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B701,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(1),IH1,VEC1)
      CALL MPMAT(WOR1,VEC1,B701,M,M,N,0)
      J=0
      CALL JACOB(J)
      CALL MPMAT(WORK,B702,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B702,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(2),IH2,VEC1)
      CALL MPMAT(WOR1,VEC1,B702,M,M,N,0)
      J=1
      CALL JACOB(J)
      CALL MPMAT(WORK,B703,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B703,M,N,M,1)
```

```
      CALL SEVENTY2(WOR3,CAL3,M,IH49(3),IH3,VEC1)
      CALL MPMAT(WOR1,VEC1,B703,M,M,N,0)
      J=2
      CALL JACOB(J)
      CALL MPMAT(WORK,B704,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B704,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(4),IH4,VEC1)
      CALL MPMAT(WOR1,VEC1,B704,M,M,N,0)
      J=3
      CALL JACOB(J)
      CALL MPMAT(WORK,B705,G,M,N,N,0)
      CALL MPMAT(WOR3,WORK,B705,M,N,M,1)
      CALL SEVENTY2(WOR3,CAL3,M,IH49(5),IH5,VEC1)
      CALL MPMAT(WOR1,VEC1,B705,M,M,N,0)
      J=4
      CALL JACOB(J)
      WRITE(2,320)
      XEEE=0.0
      DO 325 I=1,M2
      WOR1(1)=1302.9*SQRT(ABS(CAL1(I)))
      IF(CAL1(I)) 266,267,267
  267 XE=1302.9*SQRT(OBS(I))
      J=(ISS+3)*(I-1)+I00+3
      EX(J)=WOR1(1)
      XEE=WOR1(1)-XE
      XEEE=XEEE+ABS(XEE)
      WRITE(2,330)I,XE,WOR1(1),XEE
  325 CONTINUE
      XEEE=XEEE/M2
      OI(I00+1)=XEEE
      WRITE(2,380)XEEE
   14 CONTINUE
      DO 75 I=1,IC
      J=(I-1)*(ISS+2)+1
      L=INT(FPOT(J))
```

```
      J1=J+1
      J2=J1+ISS
      WRITE(2,680)L,(FPOT(J),J=J1,J2)
   75 CONTINUE
      DO 76 I=1,M2
      J=(I-1)*(ISS+3)+1
      L=INT(EX(J))
      J1=J+1
      J2=J1+ISS+1
      WRITE(2,690)L,(EX(J),J=J1,J2)
   76 CONTINUE
```

```
      INO=ISS
      CALL MINI(OI,INO,KKK)
      ISS1=INO+1
      WRITE(2,2040)KKK,(OI(I),I=1,ISS1)
      DO 18 I=1,IRE
      XPOT(I)=XINIT(I)
   18 CONTINUE
      WRITE(2,610)(XPOT(I),I=1,IRE)
      IF(IC31-4049) 551,19,551
  551 IF(IS-IK) 7,74,74
      GO TO 74
   19 DO 21 I=1,IC
      IP=ICO(I)
      K=KKK+(I-1)*(ISS+2)+1
      XINIT(IP)=FPOT(K)
      XPOT(IP)=XINIT(IP)
   21 CONTINUE
      WRITE(2,610)(XPOT(I),I=1,IRE)
      GO TO 551
  264 WOR1(1)=-WOR1(1)
      GO TO 265
  266 WOR1(1)=-WOR1(1)
        GO TO 267
   74 WRITE(2,10)N
      STOP
      END
```

```
      SUBROUTINE JACOB(J)
      DIMENSION W(144),Y(315),ID(30),IZ(200),IAR(30),ICO(20),CAL1(45),
     1CAL3(45)
      COMMON W,Y,ID,IZ,M,IAR,ICO,N,IC,MISM,CAL1,CAL3
  100 FORMAT(10I5)
  200 FORMAT(/(9F8.4))
      M=N-3
      MN=M+N
      ICM=IC*M
      DO 2 JJ=1,M
      DO 3 I=1,IC
      KK=MISM*(I-1)+JJ+J*M
      K=ICO(I)
      NO=IAR(K)
      LM=2
      ISI=1
      NA=ID(K)
      IF(IZ(NO).EQ.IZ(NO+1)) LM=1
      Y(KK)=0.0
      DO 921 JI=1,NA
      MD=IZ(NO)
      MS=IZ(NO+1)
      IF(MD.LT.0) ISI=-1
      IF(MD.LT.0) MD=-MD
      IM=N*(JJ-1)+MD
      IN=N*(JJ-1)+MS
      Y(KK)=Y(KK)+ISI*(W(IM)*W(IN))
      NO=NO+2
      ISI=1
  921 CONTINUE
      Y(KK)=LM*Y(KK)
      LM=2
    3 CONTINUE
    2 CONTINUE
      JJJ=J*M
      DO 7 I=1,M
      L=JJJ+I
      CAL1(L)=CAL3(I)
    7 CONTINUE
      RETURN
      END

      SUBROUTINE MPMAT(D,A,B,I1,I2,I3,L)
      DIMENSION D(144),A(144),B(144)
      IK=1
      DO 1 I=1,I1
      DO 2 J=1,I3
      D(IK)=0.0
      DO 3 K=1,I2
      IF(L.EQ.1) GO TO 4
      II=I3*(K-1)+J
    5 IJ=I2*(I-1)+K
      D(IK)=D(IK)+A(IJ)*B(II)
    3 CONTINUE
      IK=IK+1
    2 CONTINUE
    1 CONTINUE
      GO TO 6
    4 II=I2*(J-1)+K
      GO TO 5
    6 RETURN
      END
```

Appendix II

Figure (A - 1)

Cartesian displacement figures calculated for parabenzoquinone-h_4 using the force field parameters given in table (Q- IX-A, No. 5). The numbers relate the individual figures to the frequencies given in table (Q- VIII-B). Yhe displacements of the hydrogen atoms were scaled down by a factor, 0.20.

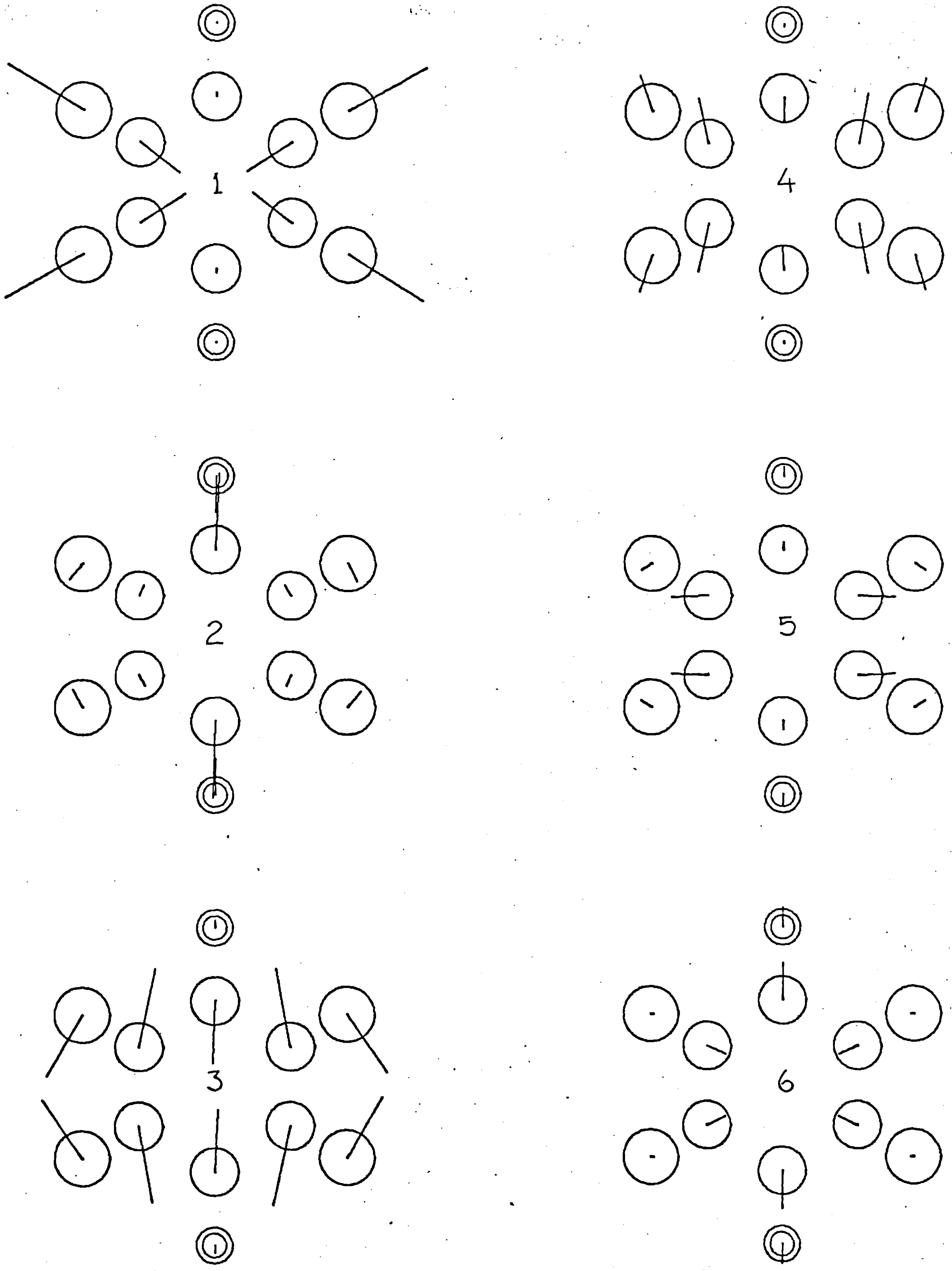
Figure (A - 2)

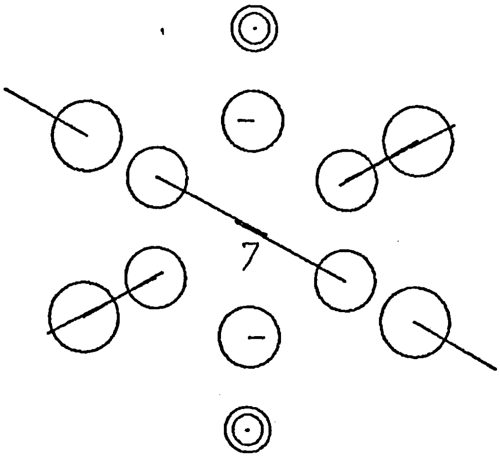
X-Y plane projections of the non-planar Cartesian displacements of parabenzoquinone-h_4, calculated using the force constants given in table (Q- XXVI; set II -A). Displacements involving oxygen atoms have been scaled up by a factor, 3.8 , and modes 7, 8, and 9, have been scaled up by a factor of 2.0.

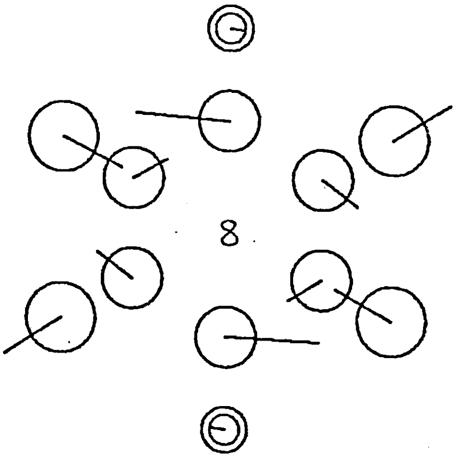
Figure (A - 3)

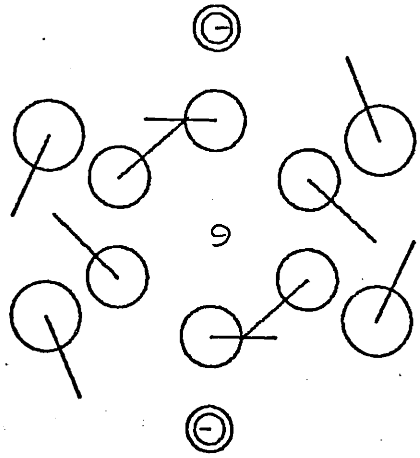
Projections of the non-planar Cartesian displacements of paradichlorobenzene, calculated using the force constants given in table (Q- XVII; set SVFF-I). Displacements of the chlorine atoms have been scaled up by a factor of 3.8.

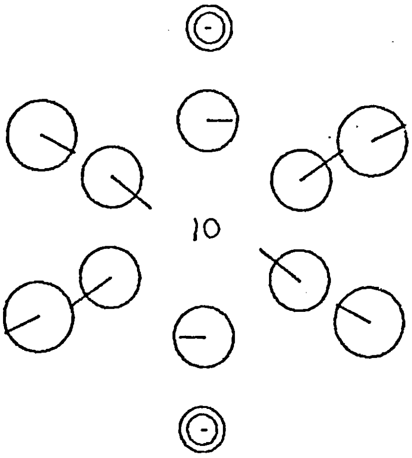
Figure (A-1)











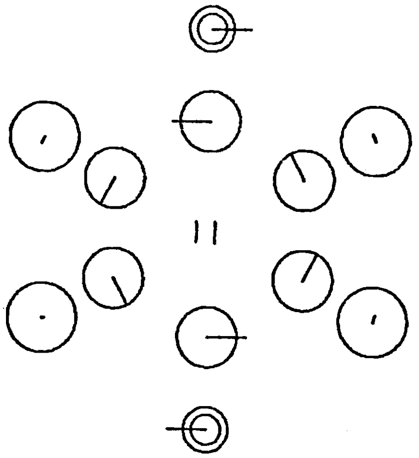
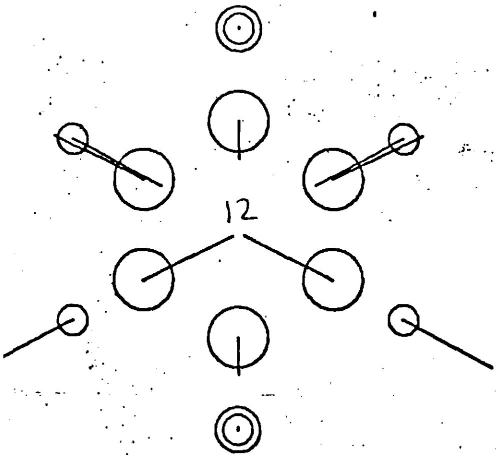
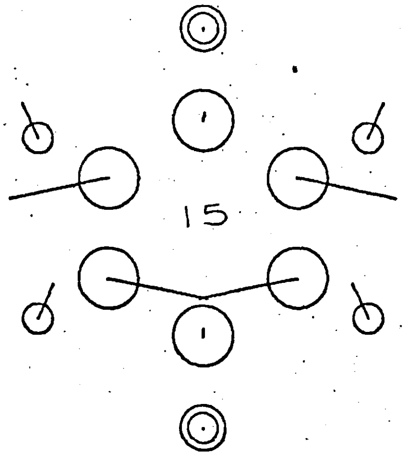
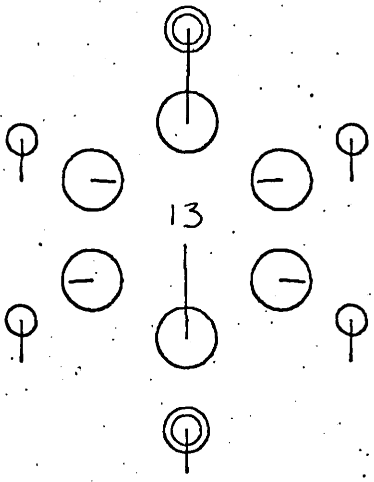
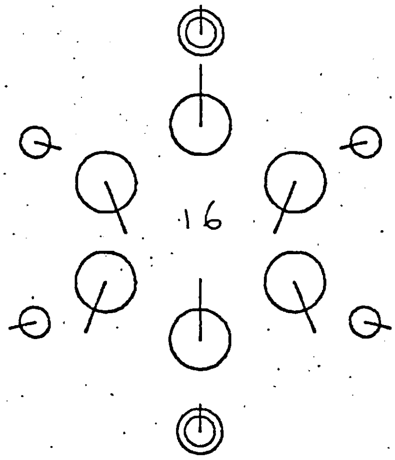


Figure (A-1) Cont.









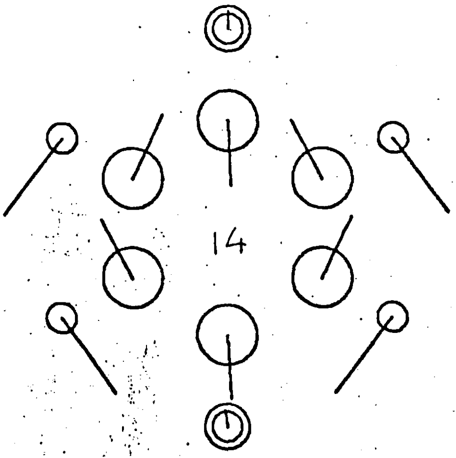


Figure (A-1) Cont.

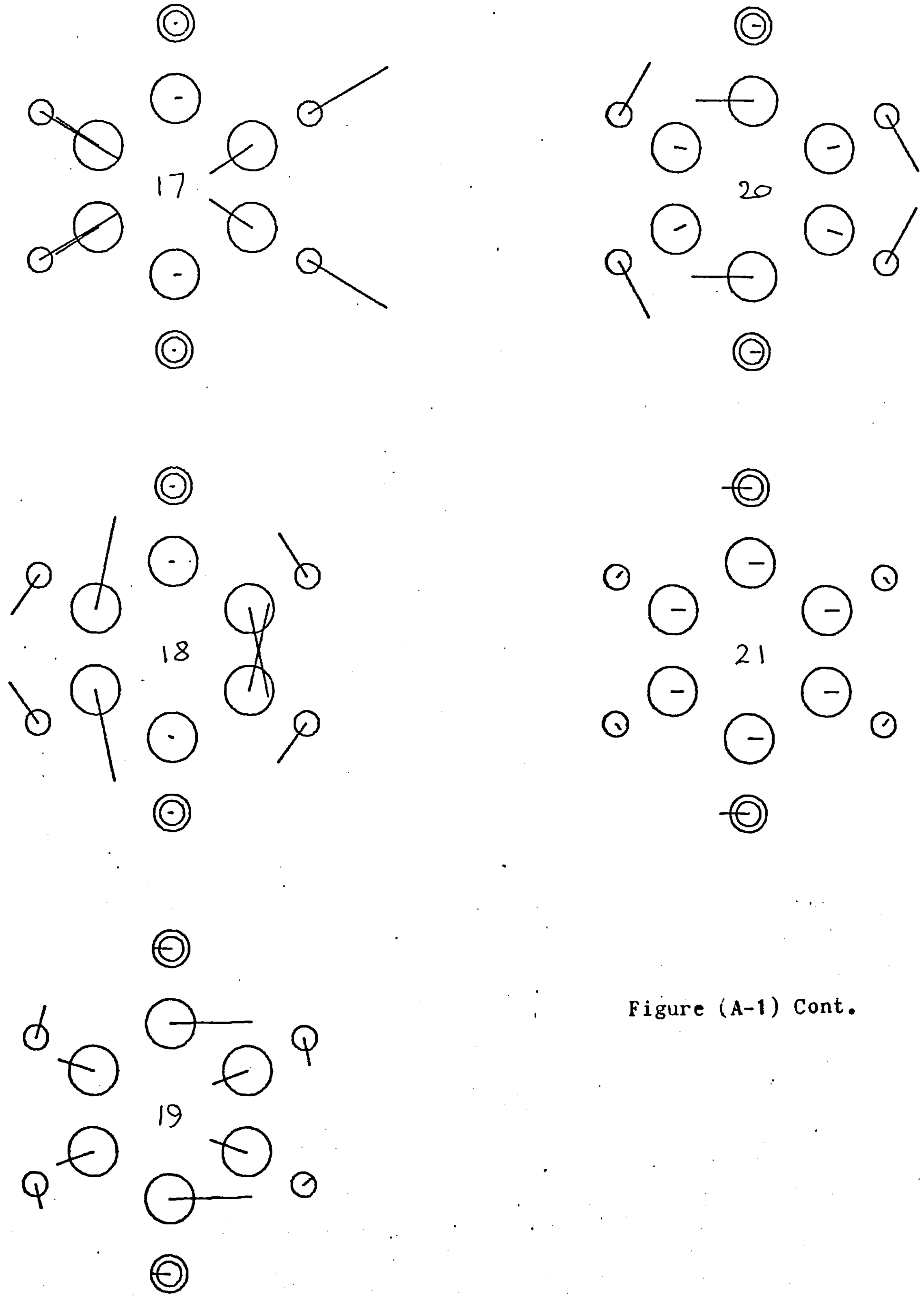
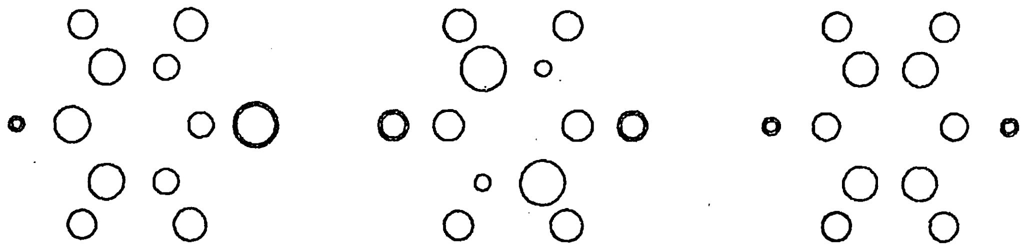
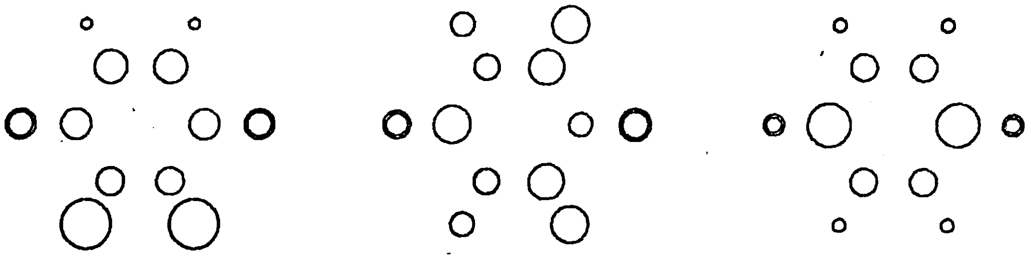


Figure (A-1) Cont.

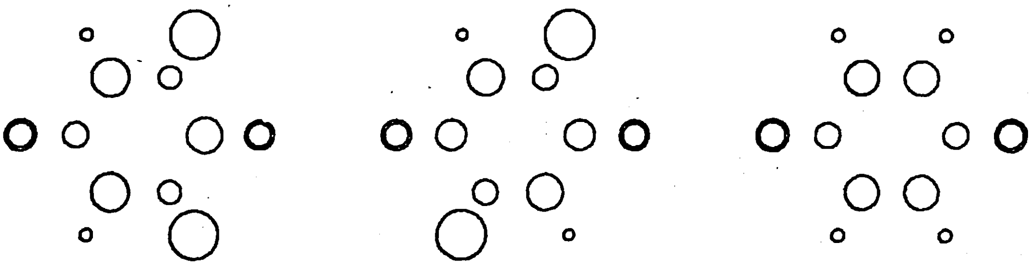
Figure (A-2)



7: B3G 0 243 C 241 8: A U 0 310 C 311 9: B1U 0 105 C 108

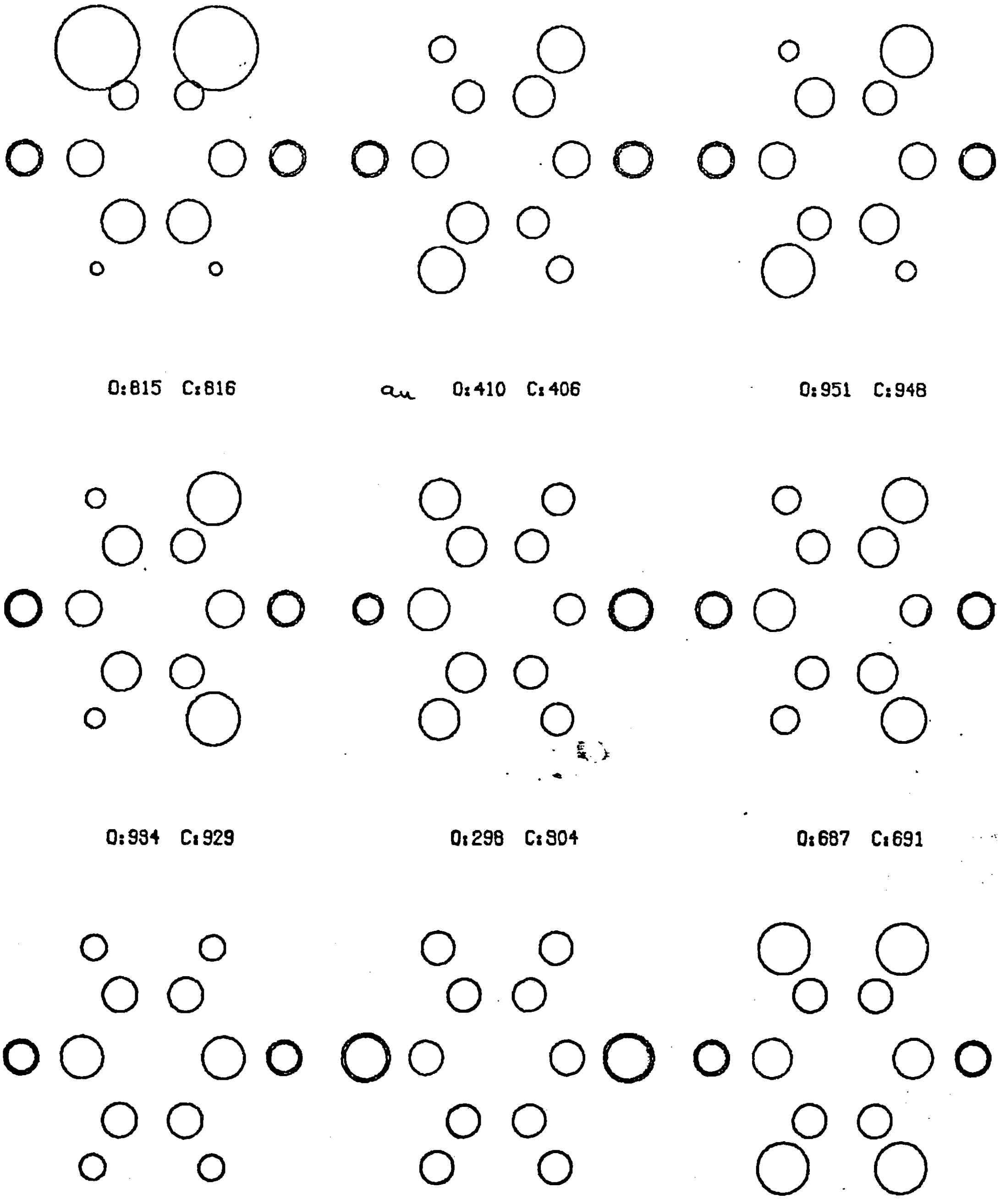


4: B2G 0 745 C 747 5: B3G 0 794 C 792 6: B1U 0 505 C 506



1: B3G 0 998 C 997 2: A U 0 969 C 968 3: B1U 0 882 C 882

Figure (A-3)



b2g O:815 C:816

au O:410 C:406

O:951 C:948

b3g O:934 C:929

O:298 C:304

O:687 C:691

b1u O:485 C:499

O:125 C:107

O:819 C:819